# Organic Reactions

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# PREFACE TO THE SERIES

In the course of nearly every program of research in organic chemistry the investigator finds it necessary to use several of the better-known synthetic reactions. To discover the optimum conditions for the application of even the most familiar one to a compound not previously subjected to the reaction often requires an extensive search of the literature, even then a series of experiments may be necessary. When the results of the investigation are published, the synthesis, which may have required months of work, is usually described without comment. The background of knowledge and experience gained in the literature search and experimentation is thus lost to those who subsequently have occasion to apply the general method. The student of preparative organic chemistry faces similar difficulties. The textbooks and laboratory manuals furnish numerous examples of the application of various syntheses, but only rarely do they convey an accurate conception of the scope and usefulness of the processes.

For many years American organic chemists have discussed these problems. The plan of compiling critical discussions of the more important reactions thus was evolved. The volumes of *Organic Reactions* are collections of chapters each devoted to a single reaction, or a definite phase of a reaction, of wide applicability. The authors have had experience with the processes surveyed. The subjects are presented from the preparative viewpoint, and particular attention is given to limitations, interfering influences, effects of structure, and the selection of experimental techniques. Each chapter includes several detailed procedures illustrating the significant modifications of the method. Most of these procedures have been found satisfactory by the author or one of the editors, but unlike those in *Organic Syntheses* they have not been subjected to careful testing in two or more laboratories. When all known examples of the reaction are not mentioned in the text, tables are given to list compounds which have been prepared by or subjected to the reaction. Every effort has been made to include in the tables all such compounds and references, however, because of the very nature of the reactions discussed and their frequent use as one of the several steps of syntheses in which not all of the intermediates have been isolated, some instances may well have been missed. Nevertheless, the investigator will be able

to use the tables and their accompanying bibliographies in place of most or all of the literature search so often required.

Because of the systematic arrangement of the material in the chapters and the entries in the tables, users of the books will be able to find information desired by reference to the table of contents of the appropriate chapter. In the interest of economy the entries in the indices have been kept to a minimum, and, in particular, the compounds listed in the tables are not repeated in the indices.

The success of this publication, which will appear periodically, depends upon the cooperation of organic chemists and their willingness to devote time and effort to the preparation of the chapters. They have manifested their interest already by the almost unanimous acceptance of invitations to contribute to the work. The editors will welcome their continued interest and their suggestions for improvements in *Organic Reactions*.

# CHAPTER 1

# HYDRATION OF OLEFINS, DIENES, AND ACETYLENES VIA HYDROBORATION

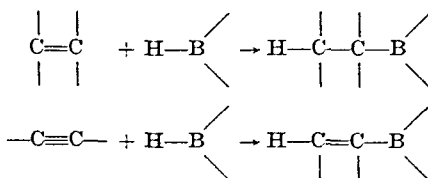GEORGE ZWEIFEL AND HERBERT C. BROWN

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## CONTENTS

1

## INTRODUCTION

The hydroboration of olefins, dienes, and acetylenes involves the addition
of a boron-hydrogen bond to the carbon-carbon multiple bond.[1,2]   This

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[1] Brown and Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); **81**, 6423, 6428 (1959);
*J. Org. Chem.*, **22**, 1136 (1957).

[2] Brown and Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959); **83**, 3834 (1961).

reaction provides a new convenient route to the corresponding organo-boranes and makes them readily available as intermediates in organic synthesis. One of the important reactions which the organoboranes undergo is the rapid and essentially quantitative oxidation with alkaline hydrogen peroxide.

$$H-C-C-B + H_2O_2 \xrightarrow{OH^-} H-C-C-OH + HOB$$

$$H-C=C-B + H_2O_2 \xrightarrow{OH^-} H-C-C=O + HOB$$
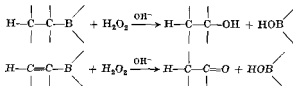
The hydroboration of olefins involves a *cis* addition of the boron-hydrogen bond, the boron atom becoming attached to the less substituted of the two olefinic carbon atoms of the double bond Furthermore the oxidation occurs with retention of configuration, placing the hydroxyl group at the precise position occupied by the boron atom in the initial organoborane Both the hydroboration and the oxidation reactions appear to be free of the carbon skeleton rearrangements that occasionally accompany other hydration procedures As a result, hydroboration followed by oxidation with alkaline hydrogen peroxide has become an important new synthetic method for the anti-Markownikoff, *cis* hydration of double bonds

This chapter surveys the available information on the hydration of olefins, dienes, acetylenes, and their derivatives by the hydroboration-oxidation procedure *

Early observations on the reaction of diborane with olefins indicated that the reaction required elevated temperatures and long reaction periods[2] and did not provide a convenient route to organoboranes Later it was observed that anhydrous aluminum chloride enhanced the reducing power of sodium borohydride to the point where the reagent at room temperature readily reduced substances such as nitriles and esters, groups which are normally resistant to sodium borohydride itself [3] Even more unexpected was the observation that olefins reacted with the reagent, utilizing one B-H equivalent per molecule of olefin and forming an organoborane [4]

$$9RCH=CH_2 + 3NaBH_4 + AlCl_3 \rightarrow 3(RCH_2CH_2)_3B + AlH_3 + 3NaCl$$
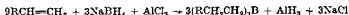
* Another survey is to be found in an article by Brown, *Tetrahedron*, **12**, 117 (1961), and a detailed discussion of the hydroboration reaction and of the synthetic applications of the resulting organoboranes is given by Brown, *Hydroboration*, W A Benjamin, New York, 1962

[2] Hurd, *J Am Chem Soc*, **70**, 2053 (1948), Stone and Eméleus, *J Chem Soc*, 1950, 2755, Whatley and Pease, *J Am Chem Soc*, **76**, 835 (1954), Stone and Graham, *Chem & Ind (London)*, 1955, 1181

[3] Brown and Subba Rao, *J Am Chem Soc*, **78**, 2582 (1956), **81**, 6423 (1959)

This discovery led to the search for alternative procedures for hydroboration. It was found that hydroboration could readily be achieved by treating an olefin with sodium borohydride and boron trifluoride in an appropriate solvent.

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3{:}O(C_2H_5)_2 \rightarrow$$
$$4(RCH_2CH_2)_3B + 3NaBF_4 + 4(C_2H_5)_2O$$
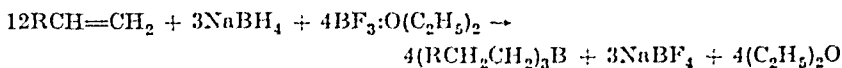
It was also discovered that, contrary to the impression given by the earlier reports, diborane itself adds rapidly and quantitatively to olefins in ether solvents.[1]

$$6RCH{=}CH_2 + B_2H_6 \rightarrow 2(RCH_2CH_2)_3B$$
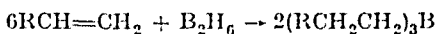
The reaction appears to be as general as the addition of hydrogen or bromine to multiple carbon-carbon bonds.

Johnson and Van Campen had noted that alkaline hydrogen peroxide effected a complete dealkylation of tri-*n*-butylborane and related organoboranes to form alcohols and boric acid.[5] A detailed study of this reaction revealed that the oxidation is essentially quantitative at 25°, that the solvents utilized for the hydroboration do not interfere with the oxidation and hence the reaction can be performed without isolating the organoborane, and that the reaction is of very wide generality.[6]

The subject matter of this chapter is limited to hydroboration-oxidation as a specific combination for the hydration of multiple carbon-carbon bonds under mild conditions. It may be noted, however, that organoboranes undergo protonolysis in the presence of carboxylic acids, providing a non-catalytic means of hydrogenating multiple carbon-carbon bonds.[7] Organoboranes also undergo coupling on treatment with alkaline silver nitrate, and this reaction provides a new synthesis for carbon-carbon bonds.[8]

### HYDROBORATION OF OLEFINS

As a result of the developments outlined above, two convenient procedures are available for the hydroboration of olefins under mild conditions: (1) treatment of a mixture of the unsaturated compound and an alkali metal borohydride in a suitable solvent with boron trifluoride etherate (or other acid), and (2) external generation of diborane followed by its reaction with the unsaturated compound in an appropriate solvent. Each of these procedures possesses advantages that will lead to its selection for specific reactions. Both procedures are described in the section on Experimental Procedures.

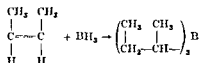[5] Johnson and Van Campen, *J. Am. Chem. Soc.*, 60, 121 (1938).

[6] H. C. Brown, C. H. Snyder, B. C. Subba Rao, and G. Zweifel, to be published.
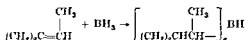
[7] Brown and Murray, *J. Am. Chem. Soc.*, 81, 4108 (1959).

[8] Brown, Hébert, and Snyder, *J. Am. Chem. Soc.*, 83, 1001 (1961); Brown and Snyder, *ibid.*, 83, 1001 (1961); Brown, Verbrugge, and Snyder, *ibid.*, 83, 1002 (1961).

## Scope and Stoichiometry

The hydroboration reaction has been applied to a large number of olefins of widely different structures. In practically all cases the reaction proceeds simply and rapidly. Only the most hindered olefins exhibit any resistance to addition. Simple olefins commonly utilize all the hydrogen atoms of diborane and form the trialkylborane.

$$C\!=\!C \begin{matrix} CH_2 \\ | \\ H \end{matrix}\begin{matrix} CH_2 \\ | \\ H \end{matrix} + BH_3 \rightarrow \left[ \begin{matrix} CH_3 & CH_3 \\ | & | \\ CH_2\!-\!CH\!- \end{matrix} \right]_3 B$$

However, trisubstituted olefins, such as 2-methyl-2-butene and 1-methyl-cyclohexene, utilize only two of the three hydrogen atoms of the borane group forming a dialkylborane.

$$(CH_3)_2C\!=\!CH\begin{matrix} CH_3 \\ | \end{matrix} + BH_3 \rightarrow \left[ \begin{matrix} CH_3 \\ | \\ (CH_3)_2CHCH\!- \end{matrix} \right]_2 BH$$

Further reaction to form a trialkylborane is very slow at room temperature. Finally, tetrasubstituted olefins, such as tetramethylethylene, react rapidly to utilize only one hydrogen atom of the borane group and form the monoalkylborane.

$$(CH_3)_2C\!=\!C\begin{matrix} CH_3 \\ | \\ | \\ CH_3 \end{matrix} + BH_3 \rightarrow (CH_3)_2CHCH\begin{matrix} CH_3 \\ | \\ | \\ CH_3 \end{matrix} BH_2$$
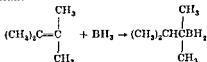
Up to the present time only two olefins, the steroids **1** and **2** (Refs 9 and 10, respectively), have been reported not to undergo hydroboration



**1**

**2**
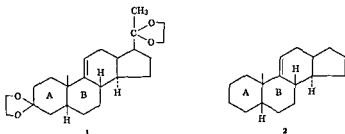
⁹ Wechter, *Chem. & Ind. (London)*, 1959, 294

¹⁰ Nussim and Sondheimer, *Chem. & Ind. (London)*, 1960, 400

On the other hand, the analogous compounds with the A/B-*trans* junction do undergo hydroboration.

The stoichiometry of the hydroboration reaction for a number of representative olefins is summarized in Table I.

<div align="center">

TABLE I

STOICHIOMETRY OF HYDROBORATION OF REPRESENTATIVE OLEFINS[1,11]

</div>

|  | Acyclic Olefins | Cyclic Olefins |
|---|---|---|
| (a) | 3 Olefin + $BH_3$ $\xrightarrow{20°}$ Trialkylborane, $R_3B$ | |
|  | 2-Methyl-1-butene | Cyclopentene |
|  | 3-Methyl-1-butene | Cyclohexene |
|  | 1-Hexene | Cycloheptene |
|  | 2-Hexene | Norbornene |
|  | 3-Hexene | $\beta$-Pinene |
|  | 4-Methyl-2-pentene | |
|  | 3,3-Dimethyl-1-butene | |
|  | 2,4,4-Trimethyl-1-pentene | |
|  | Styrene | |
|  | $\alpha$-Methylstyrene | |
|  | 1-Tetradecene | |
| (b) | 2 Olefin + $BH_3$ $\xrightarrow{20°}$ Dialkylborane, $R_2BH$ | |
|  | 2-Methyl-2-butene | 1-Methylcyclopentene |
|  | 4,4-Dimethyl-2-pentene | 1-Methylcyclohexene |
|  | 2,4,4-Trimethyl-2-pentene | $\alpha$-Pinene |
| (c) | 1 Olefin + $BH_3$ $\xrightarrow{20°}$ Monoalkylborane, $RBH_2$ | |
|  | 2,3-Dimethyl-2-butene | 1,2-Dimethylcyclopentene |
|  | 2,2,5,5-Tetramethyl-3-hexene[12] | 1,2-Dimethylcyclohexene |

### Directive Effects[13]

The oxidation of an organoborane to an alcohol by alkaline hydrogen peroxide is essentially quantitative and proceeds without rearrangement. Consequently, the structure of the alcohol formed serves to locate the position of the boron atom in the organoborane.

*Terminal olefins*, $RCH{=}CH_2$, give predominantly addition of the boron atom to the terminal carbon atom (93–94%). Thus hydroboration of 1-hexene yields an organoborane which, upon oxidation with alkaline hydrogen peroxide, is converted to a mixture composed of 94% 1-hexanol and 6% 2-hexanol. Similar results are observed with 1-butene, 1-pentene,

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[11] Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

[12] Logan and Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

[13] Brown and Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

and 1 octene, establishing the predominantly *anti*-Markownikoff direction of addition [1] Branching of the alkyl chain as in 3-methyl-1-butene, 3,3-dimethyl-1 butene, and 4,4 dimethyl-1 pentene makes no essential difference in the direction of addition

The presence of an alkyl substituent in the 2 position increases the directive effect The boron atom adds to the terminal position of olefins such as 2-methyl-1-butene to the extent of 99%

TABLE II

*Directive Effects in the Hydroboration of Terminal Olefins at 20°*

| Olefin | Alcohol Distribution,[a] % | |
|---|---|---|
| | 1-ol | 2-ol |
| 1-Butene | 93 | 7 |
| 1-Pentene | 94 | 6 |
| 2-Methyl 1-butene | 99 | 1 |
| 3-Methyl 1 butene | 94 | 6 |
| 1 Hexene | 94 | 6 |
| 3,3 Dimethyl-1-butene | 94 | 6 |
| 4,4-Dimethyl-1-pentene | 93 | 7 |
| Styrene | 80 | 20 |
| *p*-Chlorostyrene | 65 | 35 |
| 2,4,4 Trimethyl-1-pentene | 99 | 1 |
| α-Methylstyrene | 100 | Trace |
| *p*-Methylstyrene | 82 | 18 |
| *p*-Methoxystyrene | 91 | 9 |
| Allylbenzene | 90 | 10 |

[a] The yields by gas-liquid partition chromatography were 90 ± 10%.

The addition to styrene is less selective; 80% of the styrene becomes attached to the terminal position and 20% to the secondary carbon atom Moreover, the direction of addition is strongly modified by substituents in the *para* position of the aromatic nucleus

The results are summarized in Table II

The data in Table II—specifically the facts that ethylene, isopropyl-ethylene, and *t* butylethylene give 93%, 94%, and 94%, respectively, of primary alcohol—clearly show that an increase in the bulk of the alkyl group attached to the double bond does not influence the direction of addition. These results argue against steric control of the direction of addition. The marked influence of *para* substituents on the direction of addition to styrene supports the contention that the direction of addition is controlled primarily by electronic factors.

*Dialkyl* ethylenes, RCH=CHR′, such as 2 pentene and 2 hexene, undergo addition to place the boron atom in approximately equal

amounts on the 2- and 3-carbon atoms. This is true even for molecules such as *trans*-4-methyl-2-pentene and *trans*-4,4-dimethyl-2-pentene, where the two alkyl groups differ markedly in their steric requirements. Only in *trans*-1-phenylpropene, where the phenyl group is opposed to a methyl group, is a marked directive effect indicated; the boron atom becomes attached to the carbon atom holding the phenyl substituent to the extent of 85% (Table III).

### TABLE III

#### DIRECTIVE EFFECTS IN THE HYDROBORATION OF INTERNAL OLEFINS AT 20°

| Olefin | Alcohol Distribution,[a] % | |
|---|---|---|
| | 2-ol | 3-ol |
| *cis*-2-Pentene | 55 | 45 |
| *trans*-2-Pentene | 51 | 49 |
| 2-Methyl-2-butene[b] | 98[c] | 2 |
| *cis*-2-Hexene | 50 | 50 |
| *trans*-2-Hexene | 46 | 54 |
| *trans*-4-Methyl-2-pentene | 57 | 43 |
| *trans*-4,4-Dimethyl-2-pentene[b] | 58 | 42 |
| 2,4,4-Trimethyl-2-pentene[b] | 2 | 98[d] |
| *trans*-1-Phenylpropene | 85[e] | 15[f] |

[a] The yields by gas-liquid partition chromatography were 90 ± 10%.
[b] The addition yields a dialkylborane.
[c] The product is 3-methyl-2-butanol.
[d] The product is 2,2,4-trimethyl-3-pentanol.
[e] The product is 1-phenyl-1-propanol.
[f] The product is 1-phenyl-2-propanol.

*Trisubstituted olefins*, $R_2C=CHR$, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, add the boron atom predominantly at the less substituted ethylenic carbon atom.
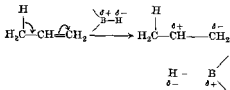
The data are summarized in Table III

Diborane undergoes *cis* addition to cyclic olefins and to acetylenes, which will be discussed later. Consequently, the addition very likely involves a four-center transition state.
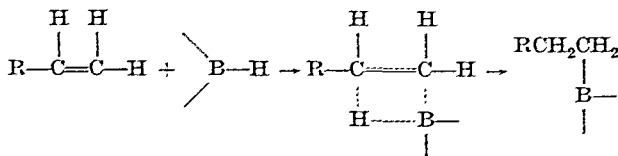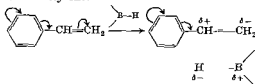


The boron-hydrogen bond is presumably polarized, the hydrogen having some hydridic character. The addition of the boron atom to the terminal position is then readily understood on the basis of the electronic shifts
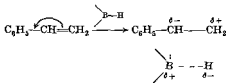
generally assumed in order to account for the normal ionic addition to propylene.

$$H_3C-CH=CH_2 \xrightarrow[B-H]{\delta+ \; \delta-} H_3C-\overset{\delta+}{CH}-\overset{\delta-}{CH_2}$$
$$\begin{array}{cc} H- & B- \\ \delta- & \delta+ \end{array}$$

A similar rationalization explains the addition of the boron atom to the terminal position of styrene.

$$C_6H_5-CH=CH_2 \xrightarrow{B-H} C_6H_5-\overset{\delta-}{CH}-\overset{\delta+}{CH_2}$$
$$\begin{array}{cc} H- & B- \\ \delta- & \delta+ \end{array}$$

It is generally recognized that a phenyl group can supply electrons to an electron-deficient center or serve as an electron sink. This provides a simple explanation for the increased substitution in the $\alpha$ position observed in styrene.

$$C_6H_5-CH=CH_2 \xrightarrow{B-H} C_6H_5-\overset{\delta-}{CH}-\overset{\delta+}{CH_2}$$
$$\begin{array}{c} B---H \\ \delta+ \quad \delta- \end{array}$$

Electron-withdrawing substituents, such as $p$-chloro, should stabilize and electron-supplying substituents, such as $p$-methoxy, should destabilize such a transition state. This conclusion is in accord with the influence of the $p$ chloro and the $p$-methoxy group on the hydroboration of substituted styrenes (Table II).

Little quantitative information is available concerning the influence of other substituents on the direction of the addition reaction. It is evident that major effects will be encountered. Trimethylvinylsilane undergoes hydroboration to place 37% of the boron atoms at the secondary position[14] as compared to 6% for 3,3-dimethyl-1-butene.[13]
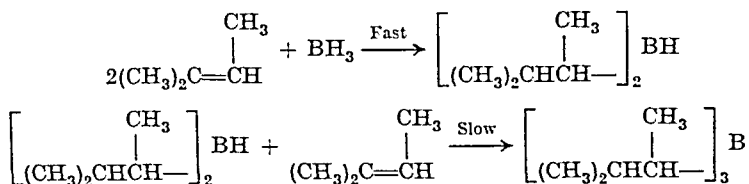
## Bis-(3-methyl-2-butyl)borane as a Selective Hydroborating Agent[15]

It was pointed out earlier that highly substituted olefins, such as 2-methyl-2-butene, undergo hydroboration rapidly to the dialkylborane

14 Seyferth, J Inorg Nucl Chem, 7, 152 (1958).
15 Brown and Zweifel, J Am Chem Soc, 83, 1241 (1961).

stage, further reaction to the trialkylborane stage being relatively slow.

$$2(CH_3)_2C\!\!=\!\!\overset{\overset{\displaystyle CH_3}{|}}{CH} + BH_3 \xrightarrow{\text{Fast}} \left[(CH_3)_2CH\overset{\overset{\displaystyle CH_3}{|}}{CH}\!\!-\right]_2 BH$$

$$\left[(CH_3)_2CH\overset{\overset{\displaystyle CH_3}{|}}{CH}\!\!-\right]_2 BH + (CH_3)_2C\!\!=\!\!\overset{\overset{\displaystyle CH_3}{|}}{CH} \xrightarrow{\text{Slow}} \left[(CH_3)_2CH\overset{\overset{\displaystyle CH_3}{|}}{CH}\!\!-\right]_3 B$$

The slowness of the last stage, in contrast to the high speed with which other olefins form the trialkylboranes, is presumably a result of the large steric requirement of the intermediate dialkylborane. It therefore

TABLE IV

DIRECTIVE EFFECTS IN THE HYDROBORATION OF UNSYMMETRICAL OLEFINS WITH DIBORANE AND WITH BIS-(3-METHYL-2-BUTYL)BORANE

| Olefin | Hydroborating Agent | Temp., °C. | Time, hr. | Alcohol Distribution, % | | |
|---|---|---|---|---|---|---|
| | | | | 1-ol | 2-ol | 3-ol |
| 1-Hexene | Diborane | 25 | 1 | 94 | 6 | |
| | R$_2$BH[a] | 0 | 1 | 99 | 1 | |
| cis-4-Methyl-2-pentene | R$_2$BH[a] | 25 | 12 | | 97 | 3 |
| trans-4-Methyl-2-pentene | Diborane | 25 | 1 | | 57 | 43 |
| | R$_2$BH[a] | 25 | 12 | | 95 | 5 |
| Styrene | Diborane | 25 | 1 | 80 | 20 | |
| | R$_2$BH[a] | 25 | 2 | 98 | 2 | |
| p-Methoxystyrene | Diborane | 25 | 1 | 91 | 9 | |
| | R$_2$BH[a] | 25 | 2 | 98 | 2 | |

[a] R$_2$BH is $\left[(CH_3)_2CH\overset{\overset{\displaystyle CH_3}{|}}{CH}\!\!-\right]_2$ BH.

appeared that this dialkylborane might exhibit an enhanced sensitivity to the steric requirement of the substituents on double bonds of other olefins and thereby exert a steric influence on the direction of hydroboration.

The reagent, bis-(3-methyl-2-butyl)borane, reacted rapidly with 1-hexene, and oxidation of the product yielded 1-hexanol in an isomeric purity of at least 99 %, in contrast to the 94 % isomeric purity realized with diborane itself. Similarly, styrene yielded less than 2 % of the secondary alcohol, in contrast to 20 % formed in the corresponding reaction with diborane. Finally, cis-4-methyl-2-pentene gave 97 % of the less hindered isomer, 4-methyl-2-pentanol.

The experimental data are summarized in Table IV.

In these studies the ease with which different olefins reacted with bis-(3-methyl-2-butyl)borane was found to vary enormously. Thus the reaction with 1-hexene was complete in a matter of minutes at 0°, whereas

internal olefins reacted much more slowly, cyclopentene reacting faster than *cis*-2-hexene and the latter reacting considerably faster than cyclohexene *cis*-2-Hexene also reacted considerably faster than the *trans* isomer Trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclohexene, reacted very slowly.

The results may be expressed in the following series of relative rates of reaction. 1-hexene > 3-methyl-1-butene > 2-methyl-1-butene > 3,3-dimethyl-1-butene > *cis*-2-hexene > cyclopentene > *trans*-2-hexene > *trans*-4-methyl-2-pentene > cyclohexene > 1-methylcyclopentene > 2-methyl-2-butene > 1-methylcyclohexene > 2,3-dimethyl-2-butene

The differences in reactivities are quite large and can be utilized for the selective hydroboration of a more reactive olefin in the presence of a less reactive one Thus treatment of a mixture of 1-pentene and 2-pentene with a controlled quantity of bis-(3-methyl-2-butyl)borane yielded pure 2-pentene. Similar treatment of a mixture of 1-hexene and cyclohexene afforded essentially pure cyclohexene, while an equimolar mixture of cyclopentene and cyclohexane gave a product containing only minor amounts of the more reactive cyclopentene A commercial mixture of *cis*- and *trans*-2-pentene (18% *cis* and 82% *trans*) with the reagent gave a product that contained more than 97% of the *trans* isomer

In contrast to the results achieved with acyclic olefins, no significant directive effect was noted in the hydroboration of 3-methylcyclopentene, 3-methylcyclohexene, or 3,3-dimethylcyclohexene [11]

In a rigid cyclic system, selective reaction was observed Treatment of 1-cholestene with bis-(3-methyl-2-butyl)borane resulted in the predominant formation of cholestan-2α-ol, in contrast to the nearly 1.1 mixture of cholestan-1α-ol and cholestan 2α-ol obtained with diborane [18]
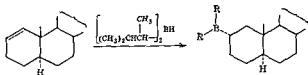


## Asymmetric Synthesis

The remarkable selectivity of a dialkylborane in hydroboration is further illustrated by the application of these olefins to optically active alcohols [17] Hydroboration of α-pinene ($[\alpha]_D + 47°$) gives diisopinocampheylborane.[11] This reagent was utilized for the hydroboration of *cis*-2-butene, *cis*-3-hexene, and norbornene Oxidation of the resulting organoborane with

[16] Sondheimer and Nussim, *J. Org Chem*, **26**, 630 (1961)

[17] Brown and Zweifel, *J Am Chem. Soc*, **83**, 486 (1961)
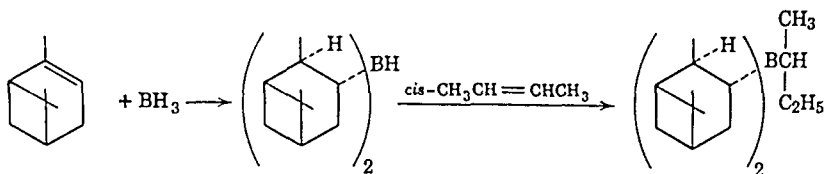
alkaline hydrogen peroxide produced the corresponding alcohols in optical purities of 70–90 %. It is noteworthy that the alcohols obtained from the hydroboration of acyclic *cis*-olefins with the diisopinocampheylboranes derived from (+) or (−) α-pinene have the R and S configurations, respectively. *trans*-Olefins and hindered olefins react only slowly with diisopinocampheylborane.

Negligible racemization of the asymmetric organoborane was observed when it was kept for several hours at room temperature.[18]

## Stereochemistry

The hydroboration of cyclic olefins provides a means of determining the stereochemistry of the reaction.[11] Thus the hydroboration of 1-methyl-cyclopentene and 1-methylcyclohexene, followed by oxidation with alkaline hydrogen peroxide, results in the formation of almost pure *trans*-2-methylcyclopentanol and *trans*-2-methylcyclohexanol, respectively. The available evidence indicates that the hydrogen peroxide oxidation proceeds with retention of configuration. Consequently, the hydroboration must involve a *cis* addition of the hydrogen-boron bond to the olefinic linkage.
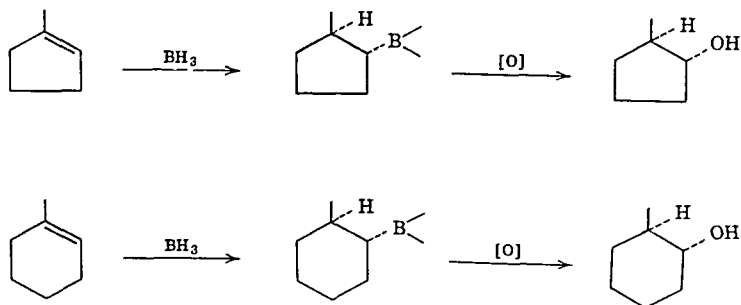


The products of these reactions are the thermodynamically more stable isomers. However, thermodynamic stability of the product cannot be

[18] H. C. Brown, N. R. Ayyangar and G. Zweifel, to be published.

the controlling factor in the reaction because the hydroboration of 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene produces the thermodynamically less stable isomers, pure *cis*-1,2-dimethylcyclopentanol and *cis*-1,2-dimethylcyclohexanol, respectively
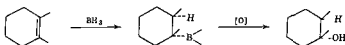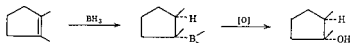




The hydroboration of norbornene proceeds to give *exo*-norborneol almost exclusively  Similarly the hydroboration-oxidation of isodrin occurs from the less hindered side [19] [20]
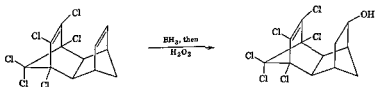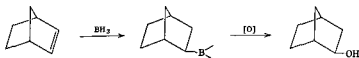




The generalization that hydroboration proceeds by *cis* addition from the less hindered side of the double bond is now supported by a considerable number of observations  α-Pinene is readily converted to isopinocampheol, β-pinene to *cis* myrtanol, and cholesterol to cholestane-3β,6α-diol [9]

[19] Cookson and Crundwell, *Chem  d  Ind  (London)*, **1959**, 703,  Bird, Cookson, and Crundwell, *J  Chem  Soc*, **1961**, 4809

[20] Bruck, Thompson, and Winstein, *Chem  d  Ind  (London)*, **1960**, 405.
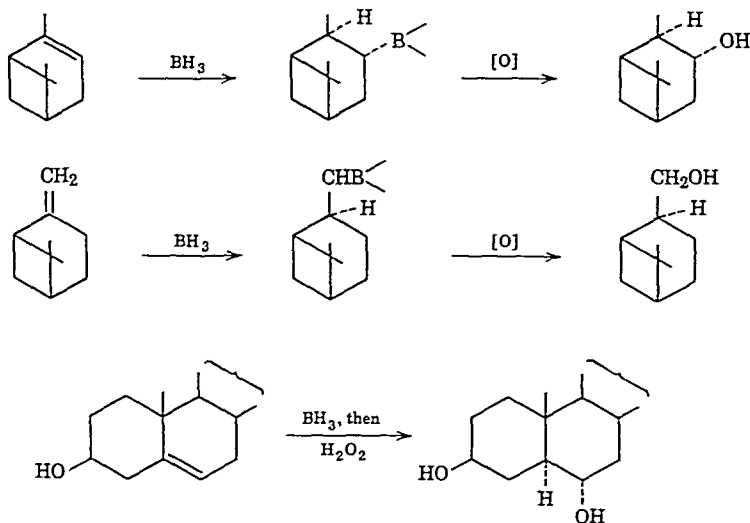
## Isomerization of Organoboranes

A simple synthetic route to primary organoboranes involves the iso-
merization of organoboranes derived from internal olefins. Secondary and
tertiary organoboranes, synthesized by means of the Grignard reaction,
slowly isomerize at 200–215° to yield primary organoboranes.[21] The
isomerization is far more rapid under hydroboration conditions. Thus
tri-2-hexylborane is almost completely isomerized to tri-n-hexylborane in
one hour at 160° in diglyme solution.[1,22]
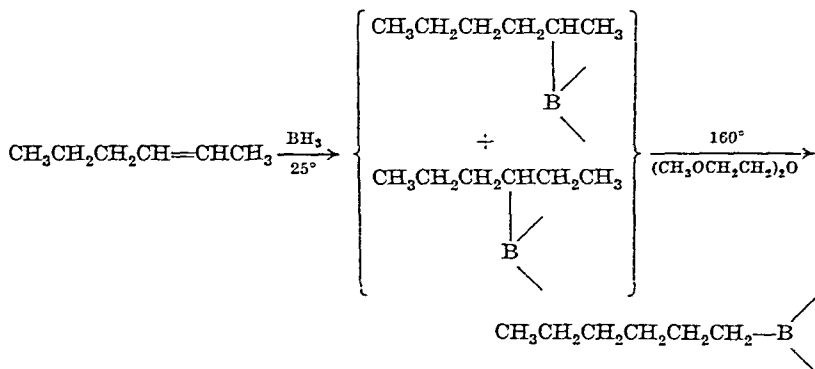
[21] Hennion, McCusker, Ashby, and Rutkowski, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

[22] Brown and Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

The small quantities of excess diborane produced in the hydroboration stage markedly catalyze the isomerization [23] Typical results are summarized in Table V.

### TABLE V

#### ISOMERIZATION OF ORGANOBORANES AT 160° [23]

| Olefin | Location of the Boron[a] | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Initially at 25°, % | | After 1 hr. at 160°, % | | | |
| | 2 | 3 | 1 | 2 | 3 | 4 |
| $\left(\begin{smallmatrix} C'-C-C-C' \\ 1\ 2\ 3\ 4 \end{smallmatrix}\right)$ | | | | | | |
| C—C=C—C—C | 52 | 48 | 95 | 4 | 1 | |
| C—C=C—C—C—C | 46 | 54 | 91 | 6 | 3 | |
| $\begin{smallmatrix} \quad C \qquad\ C \\ \quad | \qquad\ | \\ C-C=C-C-C \end{smallmatrix}$ | 1 | 99 | 97 | 1 | 2 | |
| $\begin{smallmatrix} \qquad\ C \\ \qquad\ | \\ C-C=C-C-C \\ \qquad\ | \\ \qquad\ C \end{smallmatrix}$ | 57 | 43 | 96 | 2 | 2 | |
| $\begin{smallmatrix} \quad\ C \\ \quad\ | \\ C-C=C-C \end{smallmatrix}$ | 98 | 2 | 52 | 1 | Tr. | 47 |
| C—C=C—⟨C₆H₅⟩ | 15 | 85 | 76 | 10 | 14 | |

[a] The numbers indicate the position of the boron atom, counting from the left-hand end of the chain.

The results indicate that the boron atom not only moves readily down a straight chain, but also encounters no difficulty in moving past a single alkyl branch
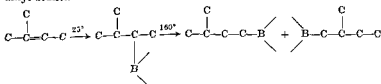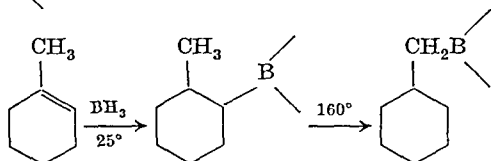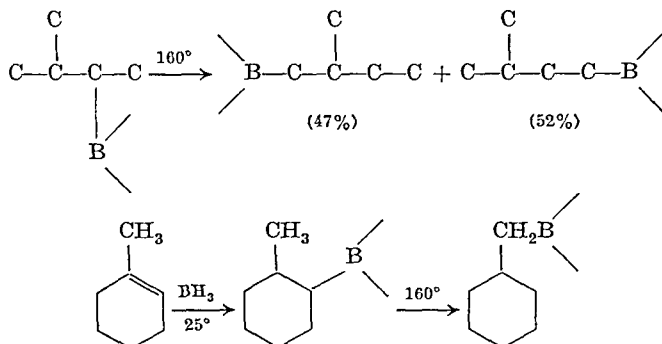


However, under the mild conditions generally used, the boron atom does not migrate past a double branch

23 Brown and Zweifel, J Am Chem Soc, 82, 1504 (1960), ibid, to be published.
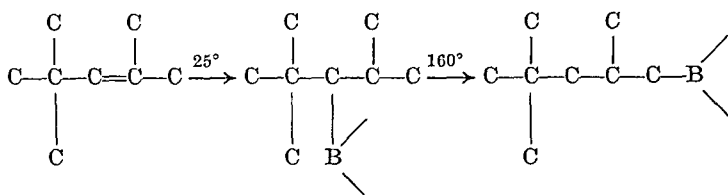
In these isomerizations, the boron atom migrates preferentially to the least hindered position in the molecule.





It is noteworthy that hydroboration of $\beta$-pinene yields the *cis*-organoborane.[11]   However, on heating, the *cis*-organoborane is converted to the more stable *trans* derivative.[24,25]
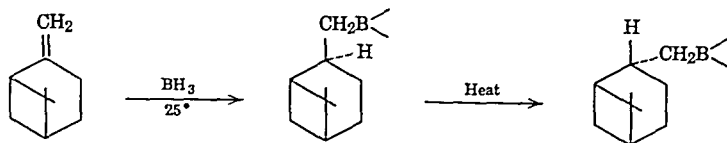


Moreover, the *trans* derivative is obtained from the hydroboration of $\alpha$-pinene followed by isomerization.[24]
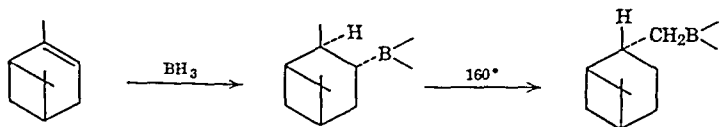


The versatility of the hydroboration reaction when coupled with thermal isomerization is illustrated by the following transformations, all of which proceed readily in yields of approximately 90%.
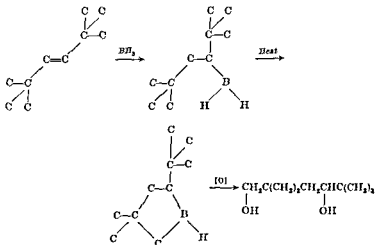
[24] H. C. Brown, M. V. Bhatt, and G. Zweifel.   Unpublished research.
[25] Braun and Fisher, *Tetrahedron Letters*, No. 21, 9 (1960).
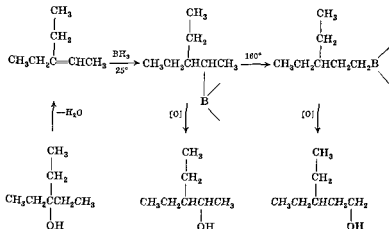
## Thermal Cyclization of Organoboranes

Certain organoboranes cyclize at elevated temperatures [12,26-28] Thus the monoalkylborane derived from *trans-di-t-butylethylene* loses hydrogen above 100° to form a cyclic organoborane  Oxidation of this cyclic product gives 2,2,5,5-tetramethyl-1,4-hexanediol [12]
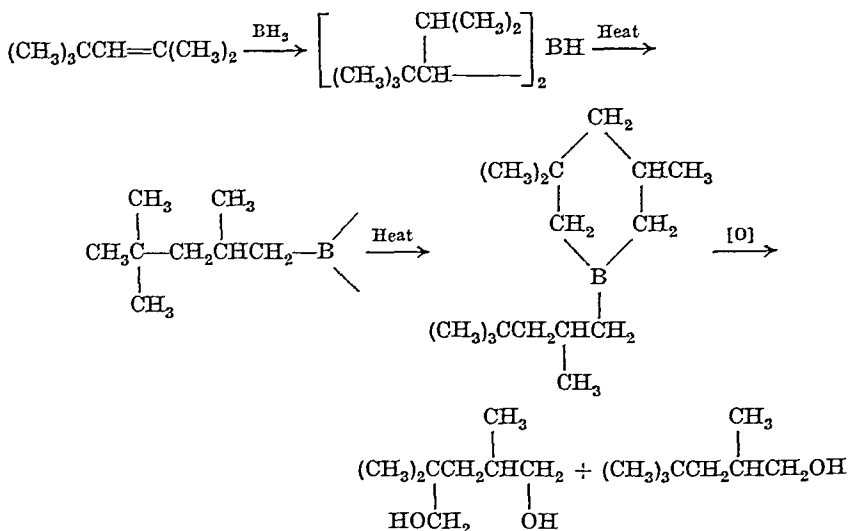
[26] Winternitz and Carotti, *J. Am Chem. Soc*, **82**, 2430 (1960).
[27] Köster and Rotermund, *Angew. Chem*, **72**, 138 (1960); **72**, 563 (1960).
[28] H  C. Brown, K. J. Murray, and G  Zweifel.  Unpublished research.

Similarly, at 160° in refluxing diglyme, bis-(2,4,4-trimethyl-1-pentyl)-borane undergoes cyclization.   Oxidation of the product yields 2,4,4-tri-methyl-1,5-pentanediol and 2,4,4-trimethyl-1-pentanol.[28]

$$(CH_3)_3CCH{=}C(CH_3)_2 \xrightarrow{\ BH_3\ } \left[ \begin{array}{c} CH(CH_3)_2 \\ | \\ (CH_3)_3CCH{-\!\!-\!\!-} \end{array} \right]_2 BH \xrightarrow{\ Heat\ }$$



$$
\begin{array}{c}
CH_2 \\
(CH_3)_2C \quad\quad CHCH_3 \\
| \quad\quad\quad | \\
CH_2 \quad\quad CH_2 \\
\diagdown \quad\quad \diagup \\
B \\
|
\end{array}
$$

$$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2\underset{CH_3}{\overset{CH_3}{C}}HCH_2{-}B \xrightarrow{\ Heat\ }$$

$$\xrightarrow{\ [O]\ }$$

$$(CH_3)_3CCH_2\underset{CH_3}{\overset{|}{C}}HCH_2$$

$$(CH_3)_2CCH_2CHCH_2 \;\dotplus\; (CH_3)_3CCH_2CHCH_2OH$$

HYDROBORATION OF DIENES

Hydroboration with Diborane

Dihydroboration of dienes followed by oxidation of the organoborane provides a route to diols.[29-32]   1,3-Butadiene is transformed into a 4:1 mixture of 1,4- and 1,3-butanediol.   Köster has assigned a cyclic structure to the organoborane derived from 1,3-butadiene.[30]

$$3CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\ 2BH_3\ }$$



$$\xrightarrow{\ [O]\ } 3HOCH_2CH_2CH_2CH_2OH$$
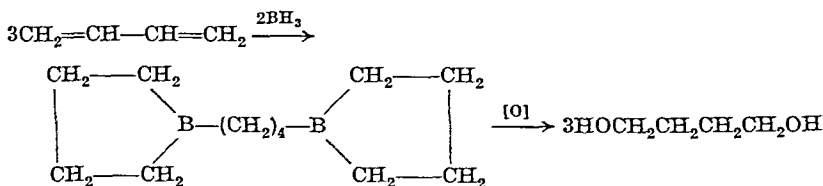
By similar procedures 1,5-hexadiene[29] and cyclopentadiene[31,32] are converted to 1,6-hexanediol and *trans*-1,3-cyclopentanediol, respectively.

[29] Brown and Zweifel, *J. Am. Chem. Soc.*, **81**, 5832 (1959); Zweifel, Nagase, and Brown, *ibid.*, **84**, 183 (1962).

[30] Köster, *Angew. Chem.*, **71**, 520 (1959).

[31] Saegebarth, *J. Am. Chem. Soc.*, **82**, 2081 (1960); *J. Org. Chem.*, **25**, 2212 (1960).

[32] Brown and Zweifel, *J. Org. Chem.*, in print.

The partial hydrogenation of dienes (monohydroboration) followed by oxidation gives the corresponding alcohols in modest yields [23] 1,5-Hexadiene is transformed into 5-hexene-1-ol, and cyclopentadiene[33] into 3-cyclopenten-1-ol. Bicycloheptadiene yields *exo*-dehydronorborneol (87 % *exo* and 13 % *endo*) [29]
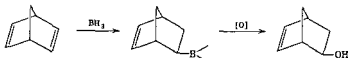


## Isomerization

Dihydroboration of acyclic dienes with diborane followed by isomerization yields cyclic organoboranes    The preferred product appears to be the 6-membered heterocycle [21]   Hydroboration of 1,3-pentadiene yields what was considered to be a mixture of bis-1,3- and bis-1,4-(1-bora-2-methylcyclopentyl)pentane, for on oxidation it furnished a 1 9 mixture of 1,3- and 1,4-pentanediol. However, the product obtained after thermal isomerization and oxidation was essentially pure 1,5-pentane-diol.[31]

$$3CH_3CH=CH-CH=CH_2 + 2BH_3 \longrightarrow$$
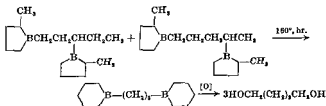


## Hydroboration with Bis-(3-methyl-2-butyl)borane

Bis-(3-methyl-2-butyl)borane has been applied to the selective hydroboration of dienes with excellent results.[15][35]   2-Methyl-1,5-hexadiene was converted in good yield to 5-methyl-5-hexen-1-ol, and 1,3-cyclohexadiene furnished a mixture consisting of 90% 2-cyclohexen-1-ol and 10% 3-cyclohexen-1-ol   Also, the more reactive double bonds in vinylcyclo-hexene, *d*-limonene, and myrcene[35] are hydrated without attack on the less reactive double bond(s).

[23] Winstein, Alfred, and Sonnenberg, *J. Am Chem. Soc.*, **81**, 3827(1959), Alfred, Sonnenberg, and Winstein, *J. Org  Chem*, **25**, 26 (1960)
[35] Zweifel, Nagase, and Brown, *J. Am Chem  Soc*, **84**, 190 (1962)
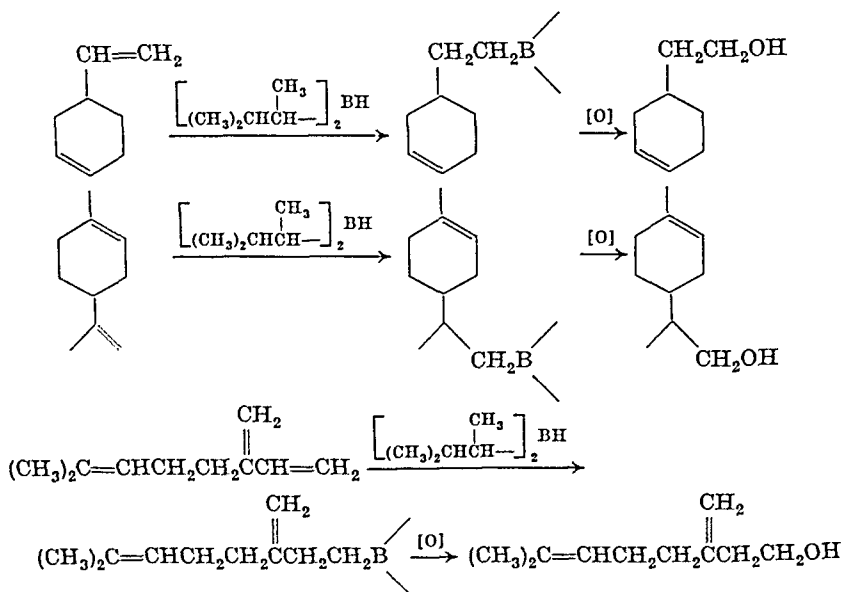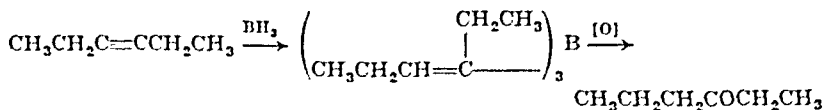
It is noteworthy that hydroboration of caryophyllene involves a preferential attack at the highly reactive *trans* internal double bond.[35]
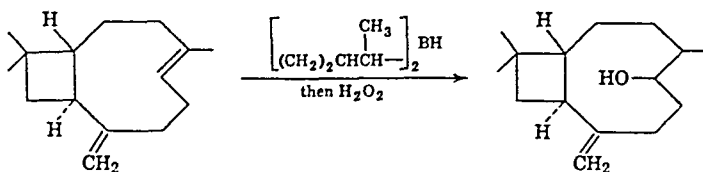
## HYDROBORATION OF ACETYLENES

Hydroboration of disubstituted acetylenes with diborane proceeds readily and can be controlled to give predominantly the vinylorganoborane. Oxidation of the latter with hydrogen peroxide affords the ketone.[2]
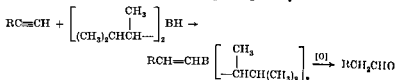
$$CH_3CH_2C\!\equiv\!CCH_2CH_3 \xrightarrow{BH_3} \left( \underset{CH_3CH_2CH=C}{\overset{CH_2CH_3}{\Big|}}\!\!- \right)_3 B \xrightarrow{[O]}$$

$$CH_3CH_2CH_2COCH_2CH_3$$

The corresponding reaction with 1-alkynes yields predominantly the dihydroboration product. However, use of either bis-(3-methyl-2-butyl)-borane or trimethylamine-*t*-butylborane[36] circumvents this difficulty and

[35] H. C. Brown and K. P. Singh, Unpublished research.
[36] Hawthorne, *J. Am. Chem. Soc.*, **83**, 2541 (1961).

results in the formation of the monohydroborated product. Oxidation of the vinylorganoborane gives the corresponding aldehyde.

$$RC\equiv CH + \left[(CH_3)_2CHCH\underset{\displaystyle |}{\overset{\displaystyle CH_3}{-}}\right]_2 BH \rightarrow$$

$$RCH=CHB\left[-CHCH(CH_3)_2\right]_2 \overset{[O]}{\longrightarrow} RCH_2CHO$$

## HYDROBORATION OF OLEFINS CONTAINING OTHER FUNCTIONAL GROUPS

Up to the present the hydroboration-oxidation reaction has been applied primarily to olefins, dienes, and acetylenes. Extension of the reaction to functional derivatives of such compounds is complicated by the reduction of many functional groups by diborane [37] [38]. Fortunately, this is not an insurmountable difficulty. The hydroboration of carbon-carbon double or triple bonds is so rapid that they can frequently be converted to organoboranes in excellent yield in the presence of such functions as acid chlorides, esters, or nitro groups. In some cases a group which is reduced very rapidly, such as the carboxyl group, can be tolerated.

For example, methyl oleate has been converted to 9- and 10-hydroxystearic acid via hydroboration.[39] Similarly bis-(3-methyl-2-butyl)borane, which reacts with but does not reduce the carboxyl group under hydroborating conditions, has been utilized to convert 10-undecenoic acid to 11-hydroxyundecanoic acid.[38]

$$H_2C=CH(CH_2)_8CO_2H + 2\left[(CH_3)_2CHCH\underset{\displaystyle |}{\overset{\displaystyle CH_3}{-}}\right]_2 BH \rightarrow$$

$$\left[(CH_3)_2CHCH\underset{\displaystyle |}{\overset{\displaystyle CH_3}{-}}\right]_2 BCH_2CH_2(CH_2)_8CO_2H\left[\overset{\displaystyle CH_3}{-CHCH(CH_3)_2}\right]_2 \overset{[O]}{\longrightarrow}$$

$$HOCH_2(CH_2)_9CO_2H$$
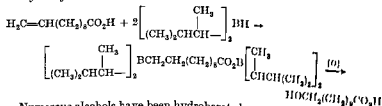
Numerous alcohols have been hydroborated, especially steroidal alcohols. The presence of one or more free hydroxyl groups requires a corresponding excess of the hydroborating agent. The boric esters formed do not interfere with the hydroboration.

$$3ROH + BH_3 \rightarrow (RO)_3B + 3H_2$$
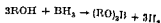
Finally, there are many functional groups that are relatively inert toward diborane or other hydroborating agents. Hydroboration of

[37] Brown and Subba Rao, *J. Am. Chem. Soc.* 82, 681 (1960); Brown and Korytnyk, *ibid.* 82, 3866 (1960).
[38] Brown and Bigley, *J. Am. Chem. Soc.* 83, 486 (1961).
[39] Fore and Bickford, *J. Org. Chem.* 24, 920 (1959).

unsaturated derivatives containing these substituents appears to offer no difficulty. The following examples are illustrative.

Vinyltrimethylsilane was readily hydroborated and converted to the corresponding alcohol.[14] Both *p*-chlorostyrene and *p*-methoxystyrene were converted to the corresponding alcohols; the *p*-substituents merely affected the ratio of the two isomeric alcohols produced.[13] Ethyl vinyl ether,[40] allyl methyl sulfide,[7] and allyl chloride[41] have been hydroborated. The organoborane derived from allyl chloride yields 3-chloropropanol on oxidation.[41] On treatment with base, however, it cyclizes to cyclopropane.[42]

## OXIDATION OF ORGANOBORANES

Whereas alkylboranes of low molecular weight are spontaneously flammable in air, tri-*n*-butylborane and higher homologs react with oxygen but do not inflame. Since air oxidation has not proved valuable in synthesis, it will not be discussed here.

Perbenzoic acid reacts practically quantitatively with tri-*n*-butylborane in chloroform solution. All three alkyl groups are cleaved with the formation of *n*-butyl alcohol and boric acid.[5]

$$R_3B + 3C_6H_5CO_3H \rightarrow B(OR)_3 + 3C_6H_5CO_2H$$
$$B(OR)_3 + 3H_2O \rightarrow 3ROH + H_3BO_3$$
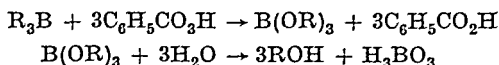
Aqueous hydrogen peroxide in the presence of dilute alkali effects a complete dealkylation of tri-*n*-butylborane.[43] The reaction was suggested as the basis of a convenient method for the determination of boron in organoboranes[5] and was later developed as an analytical procedure.[44] However, the vigorous conditions used involved heating the organoborane with excess hydrogen peroxide and concentrated sodium hydroxide under reflux.

Early applications of this reaction in the hydroboration-oxidation studies also utilized more vigorous conditions[1] than were subsequently found necessary. Hydrogen peroxide concentration, base concentration, and oxidation temperature can be varied widely without affecting the yield significantly.[6] The results are summarized in Table VI.

Standard conditions for the oxidation were defined as follows: 16.6 mmoles of tri-*n*-hexylborane in 40 ml. of diglyme was treated with 15 mmoles of sodium hydroxide (5 ml. of 3*N* solution), followed by the

[40] Mikhailov and Shchegoleva, *Bull. Acad. Sci. USSR., Div. Chem. Sci. (English Transl.)*, 1959, 518.

[41] H. C. Brown and K. Keblys. Unpublished research.

[42] Hawthorne and Dupont, *J. Am. Chem. Soc.*, 80, 5830 (1958); Hawthorne, *ibid.*, 82, 1886 (1960).

[43] Snyder, Kuck, and Johnson, *J. Am. Chem. Soc.*, 60, 105 (1938).

[44] Belcher, Gibbons, and Sykes, *Mikrochim. Acta.*, 40, 76 (1952).

TABLE VI

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION, BASE
CONCENTRATION, AND TEMPERATURE IN THE OXIDATION
OF TRI-n-HEXYLBORANE

| Hydrogen Peroxide Added, % of Theory | NaOH, mmoles | Temp., °C. | Yield, % of 1-hexanol |
|---|---|---|---|
| 72 | 45 | 25–35 | 80 |
| 95 | 45 | 25–35 | 97 |
| 120 | 45 | 25–35 | 98 |
| 150 | 45 | 25–35 | 97 |
| 100 | 45 | 25–35 | 97 |
| 100 | 30 | 25–35 | 92 |
| 100 | 15 | 25–35 | 94 |
| 100 | 0 | 25–35 | 57 |
| 100 | 45 | 0–5 | 89 |
| 100 | 45 | 25–35 | 97 |
| 100 | 45 | 50–55 | 96 |
| 100 | 45 | 75–80 | 97 |

slow addition of 60 mmoles of hydrogen peroxide, 20% excess (6.0 ml of a 30% solution). The amount of 1-hexanol obtained was determined by gas-liquid partition chromatography. The oxidation was achieved equally well in tetrahydrofuran. In diethyl ether, however, reaction was more sluggish, presumably because of the immiscibility of the solvent with water. The addition of ethanol as a cosolvent circumvented this difficulty and the yield under these conditions was 98%.[6]

As indicated in Table VII, wide variations in the structure of the organoborane do not affect the oxidation greatly.

TABLE VII

EFFECT OF STRUCTURE UPON OXIDATION

| Organoborane | Yield, % of alcohol |
|---|---|
| $\left(\bigcirc\right)_3 B$ | 97 |
| $[(CH_3)_3CCH_2CH(CH_2)CH_2-]_3B$ | 95 |
| $\left[\begin{array}{c} CH(CH_3)_2 \\ (CH_3)_2CCH---- \end{array}\right]_2 BH$ | 79 |
| $\left[\begin{array}{c} CH_3 \\ (CH_3)CHCH- \end{array}\right]_2 BH$ | 98 |
| $(C_6H_5CH_2CH_2-)_3B$ | 99 |

Numerous substances, such as olefins, dienes, acetylenes, esters, ketones, and nitriles, may be present without influencing the yield of alcohol or undergoing any reaction themselves. The results with such additives present are summarized in Table VIII.

## TABLE VIII

EFFECT OF ADDED SUBSTANCES (50 MMOLES) ON THE OXIDA-
TION OF TRI-$n$-HEXYLBORANE (16.6 MMOLES)

| Substance Added | Recovery of Added Substance After Oxidation, % | Yield, % of $n$-hexanol |
|---|---|---|
| 1-Hexene | 96 | 95 |
| 1,3-Cyclohexadiene | 96 | 95 |
| 1-Hexyne | 92 | 100 |
| Isobutyraldehyde | 63 | 97 |
| Ethyl acetate | 92 | 95 |
| $n$-Butyl bromide | 93 | 99 |
| Acetonitrile | 97 | 99 |

Although no detailed kinetic studies of the oxidation reaction of alkylboranes have been reported, Kuivila and co-workers have studied the related reaction of benzeneboronic acid with hydrogen peroxide.[45] The following mechanism was proposed.

$$H_2O_2 + {}^-OH \rightleftharpoons HO_2^- + H_2O$$

$$\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{HOB}} + {}^-O_2H \rightarrow \left[ \underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{HOB}}\!\!-\!\!OOH \right]^- \rightarrow \underset{\underset{OH}{|}}{HOBOC_6H_5} + OH^-$$
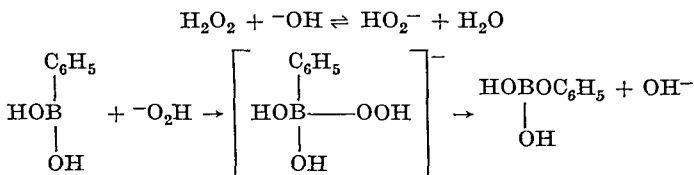
Wechter proposed an identical mechanism for the oxidation of the alkylboron bond.[9]

$$R\!-\!\underset{OH}{\overset{R}{|}}\!-\!OH \xrightarrow{\ {}^-O_2H\ } \left[ \underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{\underset{R}{\diagdown}\,B\!-\!O\!-\!OH}} \right]^- \longrightarrow \underset{\underset{OH}{|}}{RBOR} + OH^-$$
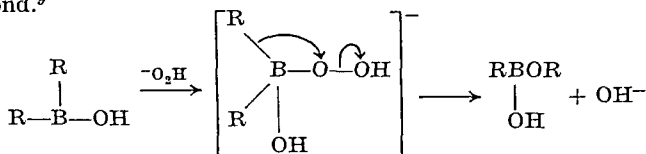
In this mechanism the group R shifts with its pair of electrons from boron to oxygen. This is consistent with the retention of configuration observed in the hydroboration-oxidation of cyclic olefins.

Organoboranes can be oxidized to ketones by chromic acid.[46] The use

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[45] Kuivila, *J. Am. Chem. Soc.*, **76**, 870 (1954); **77**, 4014 (1955); Kuivila and Wiles, *ibid.*, **77**, 4830 (1955); Kuivila and Armour, *ibid.*, **79**, 5659 (1957).

[46] Pappo, *J. Am. Chem. Soc.*, **81**, 1010 (1959).

of this reagent makes it possible to go from a cyclic olefin such as cyclohexene to the corresponding ketone, cyclohexanone, in satisfactory yield without isolating the secondary alcohol.[47]
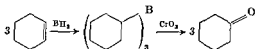


## EXPERIMENTAL CONDITIONS

The preparation and handling of organoboranes require techniques and precautions similar to those used for the Grignard reaction. Although the *necessity for a nitrogen atmosphere has not been established*, hydroboration reactions are normally carried out under nitrogen. It is convenient to transfer solutions of diborane and dialkylboranes by means of a hypodermic syringe.

Earlier reports have stressed the hazardous nature of diborane. However, during the exploration of the hydroboration reaction no difficulties have been encountered in the preparation and handling of dilute solutions of diborane and dialkylboranes. Even when solutions of diborane or dialkylboranes in tetrahydrofuran or diglyme were exposed to air, they did not inflame spontaneously but were slowly oxidized. Nevertheless, adequate ventilation is recommended.

### Hydroboration With Diborane Generated *in Situ*

In this procedure an acid is added slowly in an inert atmosphere to a *mixture of the unsaturated compound and the hydride in an appropriate solvent*. Since no diborane is liberated, the method possesses many advantages for large-scale preparations where the presence of the hydride and the inorganic product, e.g., sodium borofluoride, offers no difficulty. Therefore it is most useful when the organoborane is desired simply *as an intermediate for further reaction*.

Sodium borohydride is essentially insoluble in common ether solvents, but readily soluble in diglyme (dimethyl ether of diethylene glycol) and triglyme (dimethyl ether of triethylene glycol). Consequently, these solvents are used with sodium borohydride.[48] However, numerous procedures have been developed for utilizing metal hydrides and complex hydrides in the preparation of diborane and related reactions so as to avoid the necessity for a particular solvent or reagent.[49]

[47] Brown and Garg, *J. Am. Chem. Soc.*, 83, 2951 (1961).

[48] Brown, Mead, and Subba Rao, *J. Am. Chem. Soc.*, 77, 6209 (1955).

[49] Brown, K. J. Murray, L. J. Murray, Snover, and Zweifel, *J. Am. Chem. Soc.*, 82, 4233 (1960).

*Lithium borohydride* is readily soluble in diethyl ether and tetrahydrofuran as well as in other ether solvents. In diethyl ether the essentially quantitative hydroboration of 1-octene was achieved with boron trifluoride etherate, hydrogen chloride, and sulfuric acid. Lithium borohydride requires only sufficient boron trifluoride to convert the lithium to lithium fluoride.

$$12RCH{=}CH_2 + 3LiBH_4 + BF_3 \rightarrow 4(RCH_2CH_2)_3B + 3LiF$$
$$9RCH{=}CH_2 + 3LiBH_4 + 3HCl \rightarrow 3(RCH_2CH_2)_3B + 3LiCl + 3H_2$$
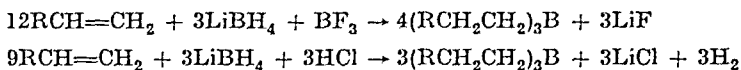
*Sodium borohydride* is soluble in diglyme and triglyme, and the hydroboration reactions with boron trifluoride etherate, hydrogen chloride, or sulfuric acid proceed rapidly and quantitatively at room temperature.

Although the solubility of sodium borohydride in tetrahydrofuran is small, the hydroboration of an olefin is readily achieved by treating with boron trifluoride a suspension of sodium borohydride in tetrahydrofuran containing the olefin.[49,50] Alternatively, a solution of diborane in tetrahydrofuran can be prepared by treating a suspension of sodium borohydride in that solvent at 0° with hydrogen chloride. Hydroboration is then accomplished by adding the olefin to this solution.

Finally, it is possible to utilize diethyl ether as the solvent by introducing 10 mole % of anhydrous zinc chloride to catalyze the reaction between sodium borohydride and boron trifluoride etherate.

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3 \xrightarrow{10\%ZnCl_2} 4(RCH_2CH_2)_3B + 3NaBF_4$$
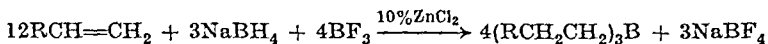
*Potassium borohydride*, although only slightly soluble in triglyme and in tetrahydrofuran, can be utilized as a suspension in these solvents. A potassium borohydride suspension in triglyme will react directly with boron trifluoride etherate, while a suspension in tetrahydrofuran will react with lithium chloride to form the soluble lithium borohydride.[51] The latter can be utilized for the hydroboration.[49]

$$KBH_4 \text{ (susp.)} + LiCl \rightarrow LiBH_4 + KCl$$
$$12RCH{=}CH_2 + 3LiBH_4 + BF_3 \rightarrow 4(RCH_2CH_2)_3B + 3LiF$$
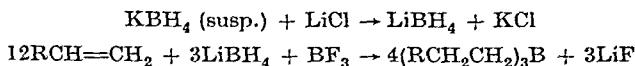
*Lithium aluminum hydride* with boron trifluoride etherate appears to be a convenient reagent for hydroboration in diethyl ether.[52,53]

$$12RCH{=}CH_2 + 3LiAlH_4 + 4BF_3 \rightarrow 4(RCH_2CH_2)_3B + 3LiAlF_4$$
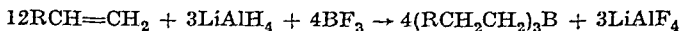
[50] Schubert and Lang, *Angew. Chem.*, **72**, 994 (1960).
[51] Paul and Joseph, *Bull. Soc. Chim. France*, **1952**, 550.
[52] Wolfe, Nussim, Mazur, and Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).
[53] Sondheimer and Wolfe, *Can. J. Chem.*, **37**, 1870 (1959).

TABLE IX

CONVENIENT PROCEDURES FOR HYDROBORATION WITH
VARIOUS HYDRIDE REAGENTS[49]

| Solvent | Hydride Source | Acid | Molar Ratio | | | 1-Octene, % reacted in 1 hr. at 25° |
|---|---|---|---|---|---|---|
| | | | Hydride : | Acid : | Olefin | |
| Diglyme | NaBH₄ | BF₃ | 3 | 4 | 12 | 99 |
| | | BCl₃ | 3 | 4 | 12 | 98 |
| | | AlCl₃ | 3 | 1 | 9 | 50 |
| | | HCl | 2 | 2 | 6 | 94 |
| | | H₂SO₄ | 3 | 1 | 6 | 91 |
| | | CH₃I | 2 | 2 | 6 | 95 |
| THF[a] | NaBH₄ | BF₃ | 3 | 4 | 12 | 99 |
| Diethyl ether | NaBH₄/ZnCl₂ | BF₃ | 3 | 4 | 12 | 94 |
| THF | KBH₄/LiCl | BF₃ | 3 | 1 | 12 | 83 |
| Diglyme | LiBH₄ | BF₃ | 3 | 4 | 12 | 98 |
| | | BCl₃ | 3 | 1 | 12 | 92 |
| THF | LiBH₄ | BF₃ | 3 | 1 | 12 | 99 |
| | | HCl | 2 | 2 | 6 | 95 |
| | | H₂SO₄ | 2 | 1 | 6 | 99 |
| Diethyl ether | LiBH₄ | BF₃ | 3 | 1 | 12 | 87 |
| | | HCl | 2 | 2 | 6 | 95 |
| | | H₂SO₄ | 2 | 1 | 6 | 92 |
| | LiAlH₄ | BF₃ | 3 | 4 | 12 | 80[b] |
| | | BCl₃ | 3 | 4 | 12 | 95 |
| Diglyme | NaH | BF₃ | 6 | 6 | 8 | 99 |
| THF | NaH | BF₃ | 6 | 8 | 6 | 99 |
| Diglyme | LiH | BF₃ | 6 | 8 | 6 | 95 |
| THF | LiH | BF₃ | 6 | 6 | 6 | 95 |
| Diethyl ether | LiH | BF₃ | 6 | 8 | 6 | 93 |
| Benzene | C₆H₅N·BH₃ | BF₃ | 1 | 1 | 3 | 90[c] |

ᵃ THF is tetrahydrofuran.
ᵇ Cyclohexene was the olefin in this experiment [53]
ᶜ This experiment was run for 16 hours at 75°.

The most convenient hydroboration procedures are summarized in Table IX. It is to be noted that lithium borohydride in tetrahydrofuran or in diethyl ether requires boron trifluoride than does sodium borohydride or lithium aluminum hydride.

## Hydroboration With Diborane Generated Externally

Hydroboration with diborane produces the organoborane in essentially quantitative yield and free of inorganic salt or other by-products. In this

procedure, diborane, prepared by the addition of sodium borohydride in diglyme to boron trifluoride etherate, is passed into a solution of the olefin in an ether solvent. Tetrahydrofuran has two distinct advantages as a reaction medium: it is an excellent solvent for diborane, and it is readily distilled from the reaction products.

Sodium borohydride in diglyme absorbs a half-molar equivalent of diborane, forming sodium diborohydride ($NaBH_4 \cdot BH_3$ or $NaB_2H_7$).[54] Because of the formation of this species, the addition of boron trifluoride etherate to a diglyme solution of sodium borohydride does not liberate diborane until nearly half of the acid has been added. Consequently, to generate diborane smoothly it is preferable to add the solution of sodium borohydride to an excess of boron trifluoride in diglyme.

$$3NaBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3NaBF_4$$
$$12RCH{=}CH_2 + 2B_2H_6 \rightarrow 4(RCH_2CH_2)_3B$$
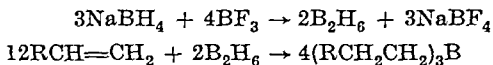
Alternatively, a $1M$ solution of diborane in tetrahydrofuran may be prepared and then utilized for the hydroboration. Such solutions can be kept at 0–5° for several weeks without significant change in the diborane concentration.

### Solvents

In order to avoid losses of active hydride in the hydroboration stage, it is important that the solvents be free of water and peroxides.

*Diglyme* (dimethyl ether of diethylene glycol, b.p. 162°) (Ansul Chemical Co.) is purified in the following way: 1 l. of diglyme is stored over 10 g. of small pieces of calcium hydride for 12 hours. The diglyme is then decanted into a distilling flask and sufficient lithium aluminum hydride is added to ensure an excess of active hydride. The solvent is distilled at 62–63°/15 mm.

*Triglyme* (dimethyl ether of triethylene glycol, b.p. 212°) is purified as described for diglyme. The solvent is distilled at 107–108°/15 mm.

*Tetrahydrofuran* (pure grade) is treated with lithium aluminum hydride as just described, then distilled at atmospheric pressure; b.p. 66–67°.

*Diethyl ether* (anhydrous reagent grade) is utilized without purification.

In order to inhibit peroxidation during storage of these solvents, it is advantageous to add 0.01 % of sodium borohydride.

### Boron Trifluoride Etherate

Boron trifluoride diethyl etherate, 500 ml., is treated with 10 ml. of anhydrous diethyl ether (to ensure an excess of this component) and

[54] Brown and Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

distilled in an all glass apparatus at 46°/10 mm. from 2 g. of granular calcium hydride  The hydride removes small quantities of volatile acids and greatly reduces bumping during the distillation  The density of the product at 25° is 1 125

## Metal Hydrides

Sodium borohydride (98%) from Metal Hydrides, Inc., may be used without purification. Commercial lithium borohydride and potassium borohydride were used without purification after analysis for active hydrogen

## EXPERIMENTAL PROCEDURES

### Procedures in Which Diborane Is Generated *in Situ*

The apparatus consists of a three-necked flask equipped with a condenser fitted with a calcium chloride tube, a pressure-equalizing dropping funnel, a thermometer, and a stirrer (a magnetic stirrer may be utilized for small-scale experiments).  The apparatus is dried in an oven and assembled under dry nitrogen  Alternatively, it can be flamed dry in a stream of dry nitrogen

To the flask are added the olefin and the hydride in an appropriate solvent.  A 10–20% excess of the hydride is generally used.  A quantity of acid, equivalent to the hydride used and generally in a solvent, is added dropwise in a nitrogen atmosphere.  After completion of the addition, the excess hydride is *carefully* decomposed by water or ethylene glycol.  The organoborane obtained can be oxidized *in situ* with alkaline hydrogen peroxide

### Isopinocampheol from α-Pinene (Use of Sodium Borohydride and Boron Trifluoride Etherate in Diglyme).[11 55]  In a 300-ml. flask are placed 82 5 ml. of a 1M solution of sodium borohydride in diglyme
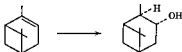


(10% excess) and 27.2 g of α-pinene (0 20 mole); $n_D^{20}$ 1 4648, $[\alpha]_D^{20}$ +46 8°) in 20 ml of diglyme  The flask is immersed in a water bath (~20°).  From the dropping funnel 14 ml of boron trifluoride etherate (15 62 g, 0 11 mole) is added dropwise to the stirred reaction mixture over a period

[55] H C Brown, K P Singh, and G Zweifel  Unpublished research

of 30 minutes, while the temperature is maintained at 20–25°. The flask is kept for 1 hour at this temperature. Excess hydride is then decomposed by the careful dropwise addition of 20 ml. of water.

The organoborane ($R_2BH$) is oxidized at 30–50° by the immediate addition of 22 ml. of $3N$ sodium hydroxide, followed by the dropwise addition of 22 ml. of 30% hydrogen peroxide. The reaction mixture is left for 1 hour at room temperature and is then extracted with 150 ml. of ether. The ethereal extract is washed five times with equal amounts of ice water to remove diglyme, and dried over anhydrous magnesium sulfate. The product obtained after removal of the solvent is crystallized from a small amount of petroleum ether (35–37°). There is obtained 24.3 g. (79%) of isopinocampheol: m.p. 55–57°, $[\alpha]_D^{20}$ −32.8° (c, 1% in benzene).

**4-Methyl-1-pentanol from 4-Methyl-1-pentene (Use of Sodium Borohydride and Boron Trifluoride Etherate in Tetrahydrofuran).**[49] To a well-stirred suspension of 3.4 g. (90 mmoles) of pulverized sodium borohydride in 150 ml. of tetrahydrofuran containing 25.2 g. of 4-methyl-1-pentene (0.30 mole; $n_D^{20}$ 1.3830) is added 15.1 ml. of boron trifluoride etherate (17.0 g., 0.120 mole) in 20 ml. of tetrahydrofuran over a period of 1 hour, while the temperature is maintained at 25°. The flask is kept an additional hour at 25° before the excess hydride is decomposed with water.

The organoborane is oxidized at 30–40° (water bath) by the addition of 32 ml. of a $3N$ solution of sodium hydroxide, followed by the dropwise addition of 32 ml. of 30% hydrogen peroxide. The reaction mixture is saturated with sodium chloride. The tetrahydrofuran layer formed is separated, and then washed with saturated aqueous sodium chloride. The extract is dried over anhydrous magnesium sulfate.

Distillation furnished, after removal of the tetrahydrofuran, 24.5 g. (80%) of 4-methyl-1-pentanol, b.p. 151–153°/735 mm; $n_D^{20}$ 1.4140.

**2,4,4-Trimethyl-1-pentanol from 2,4,4-Trimethyl-1-pentene (Use of Lithium Borohydride and Sulfuric Acid in Tetrahydrofuran).**[49] In a 500-ml. flask are placed 2.62 g. of lithium borohydride (0.12 mole), 33.6 g. of 2,4,4-trimethyl-1-pentene (0.30 mole, $n_D^{20}$ 1.4807), and 170 ml. of tetrahydrofuran. Concentrated sulfuric acid (5.88 g., 60 mmoles) in 42 ml. of diethyl ether is added over a period of 1 hour to the lithium borohydride-olefin solution, the temperature being maintained at 25°. The reaction is permitted to proceed for an additional hour at room temperature, and then the excess hydride is decomposed with water.

The organoborane is oxidized at 20–40° (water bath) by the addition of 32 ml. of a $3N$ solution of sodium hydroxide, followed by the dropwise addition of 32 ml. of 30% hydrogen peroxide. The tetrahydrofuran-ether layer is separated, washed with water, and dried over anhydrous magnesium sulfate.

The product obtained after removal of the solvent furnishes on distillation 31.6 g (81%) of 2,4,4-trimethyl-1-pentanol, b p 165–166°/748 mm , $n_D^{25}$ 1 4274.

**Cyclohexanol from Cyclohexene (Use of Lithium Aluminum Hydride and Boron Trifluoride Etherate in Diethyl Ether).[53]** In a flask are placed 3 4 g of boron trifluoride etherate (24 mmoles), 4 g of cyclohexene (49 mmoles), and 100 ml of diethyl ether. A solution of 0 7 g. (18 mmoles) of lithium aluminum hydride in 70 ml of ether is added to the olefin-boron trifluoride mixture during 20 minutes. The mixture is stirred at room temperature for 2 hours, and then the excess hydride is decomposed by slowly adding 20 ml of acetone. A saturated solution of sodium sulfate is added, followed by solid sodium sulfate. The mixture is filtered, and the clear filtrate evaporated.

The residue is dissolved in 30 ml of 90% ethanol containing 0 8 g of sodium hydroxide, and 10 2 ml of 20% hydrogen peroxide is added with stirring during 5 minutes. The temperature of the reaction mixture rises to about 70°. It is maintained at this temperature for 5 minutes longer by external heating, and the flask is then cooled. Water and ether are added, and the ether extract is washed with water, dried, and evaporated. On distillation there is obtained 4 0 g. (82%) of cyclohexanol, b p. 161–162°, $n_D^{25}$ 1 4656

## Procedures in Which Diborane Is Generated Externally (Fig. I)

*exo*-Norborneol from Norbornene.[11,55] A dry 500 ml three-necked flask is equipped with a thermometer, a condenser connected to a mercury bubbler containing acetone (T-tube dipping in mercury), and a sintered glass dispersion tube  A tube from the condenser outlet dips below the surface of some mercury in a side arm test tube  Above the mercury is a layer of acetone which serves to destroy escaping diborane by reacting with it to form diisopropoxyborane, $[(CH_3)_2CHO]_2BH$

A solution of 28 2 g (0 30 mole) of norbornene, m p  45°, in 100 ml of tetrahydrofuran is placed in the flask  The dispersion tube (completely immersed in the tetrahydrofuran olefin solution) is connected with Tygon tubing to a 300-ml two-(or three-)necked flask serving as the diborane generator

The generator is equipped with a pressure equalizing dropping funnel (serving alternatively as an inlet for nitrogen) containing 90 ml of a 1M solution of sodium borohydride in diglyme (3 4 g , 20% excess)  In the generator is placed 23 ml of boron trifluoride etherate (25 5 g , 0 18 mole, 50% excess) in 20 ml of diglyme

<sub>46</sub> H C Brown, S Nishida, and G Zweifel  Unpublished research

Diborane is generated by the dropwise addition of the sodium boro-
hydride solution to the stirred boron trifluoride etherate-diglyme solution.
The gas is passed into the olefin-tetrahydrofuran solution (maintained at
20°) by applying a slight flow of dry nitrogen through the generator.
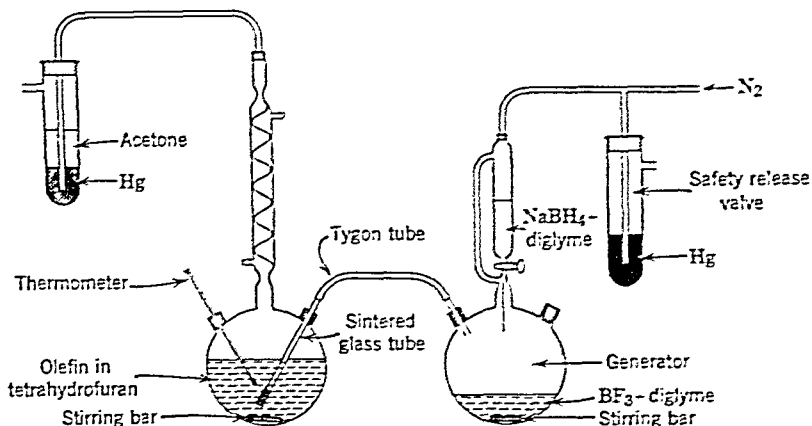


FIG. 1.

After completion of the sodium borohydride addition (1 hour), the gener-
ator is heated for 1 hour at 70–80°, the nitrogen flow being maintained
to ensure the complete transfer of the diborane to the hydroboration
flask. The generator is allowed to cool to room temperature and is then
disconnected from the hydroboration flask.

The excess hydride in the hydroboration flask is decomposed by the
careful addition of 20 ml. of water. The organoborane is oxidized at
30–50° (water bath) by the addition of 32 ml. of $3N$ sodium hydroxide,
followed by dropwise addition of 32 ml. of 30% hydrogen peroxide.
During the oxidation, efficient stirring is maintained. The reaction
mixture is stirred for an additional hour, then 100 ml. of diethyl ether is
added. The organic phase is separated, the aqueous phase is saturated
with sodium chloride and then extracted twice with 50-ml. portions of
ether. The combined extracts are washed twice with 50-ml. portions of
saturated sodium chloride solution and dried over anhydrous magnesium
sulfate.

The product obtained after removal of the solvent is crystallized from a
small amount of petroleum ether to furnish 24.4 g. (74%) of *exo*-norborneol,
m.p. 126–127° after sublimation.

**2,3-Dimethyl-1,4-butanediol from 2,3-Dimethylbutadiene (Prep-
aration and Use of a Solution of Diborane in Tetrahydrofuran).[29]**
*A. Preparation of a Solution of Diborane in Tetrahydrofuran.* The

experimental conditions and the apparatus utilized are described on p. 32

In a 1-l flask with a side arm capped by a rubber septum to permit the removal of material is placed 500 ml of tetrahydrofuran. The flask is immersed in an ice bath. Diborane, generated by the addition of 950 ml. of a 1$M$ solution of sodium borohydride in diglyme and boron trifluoride etherate (50% excess), is passed through a solution of sodium borohydride (to remove traces of boron trifluoride) into the tetrahydrofuran

Determination of the boron by titration and hydride by hydrolysis shows that the solution is ~1.0$M$ in diborane. The concentration of the diborane does not change significantly over a period of several weeks when the solution is kept under nitrogen at 0°.

*B* *Hydroboration-Oxidation* In a 300-ml. flask is placed 8.2 g. (0.10 mole) of 2,3-dimethyl-1,3-butadiene in 100 ml of tetrahydrofuran. The flask is immersed in an ice bath. Fifty milliliters of a 1$M$ solution of diborane in tetrahydrofuran is added slowly to the diene-tetrahydrofuran solution After the addition the flask is kept for 30 minutes at room temperature, and the excess hydride is decomposed by the careful addition of water

The organoborane is oxidized at 30–50° (water bath) by the addition of 24 ml. of 3$N$ sodium hydroxide, followed by the dropwise addition of 24 ml of 30% hydrogen peroxide. After 1 hour at room temperature, 75 g of potassium carbonate is added with moderate stirring The tetrahydrofuran layer is separated, and the aqueous phase extracted twice with 30-ml portions of tetrahydrofuran. The extracts are combined and dried over anhydrous magnesium sulfate.

The solvent is removed and the product is distilled The yield is 2,3-dimethyl-1,4-butanediol (b.p 105–106°/2 mm , $n_D^{20}$ 1.4563) is 7.8 g (66%)

*n*-Octanal from 1-Octyne [Preparation and Use of Bis-(3-methyl-2-butyl)borane].[3] *A.* In a three-necked flask are placed 33.6 g of 2-methyl-2-butene (0.48 mole) and 180 ml of a 1$M$ solution of sodium borohydride in diglyme. The flask is immersed in an ice bath. Boron trifluoride etherate, 0.24 mole, is added dropwise to the reaction mixture, efficient stirring being maintained. The flask is permitted to remain for 2 hours at 0° and is then placed in an ice-salt bath.

*B* To the reagent (0.24 mole) prepared in *A*, 22.0 g. (0.20 mole) of 1-octyne in 20 ml of diglyme is added as rapidly as possible while the temperature is maintained at 0–10° The reaction mixture is permitted to warm to room temperature to complete the hydroboration.

The organoborane is oxidized at 0° by the addition of 150 ml. of a 15%

solution of hydrogen peroxide, while the $pH$ of the reaction mixture is maintained at 7–8 by the controlled addition of $3N$ sodium hydroxide. The reaction mixture is then neutralized and steam distilled. The distillate is extracted with ether and the extract dried over anhydrous magnesium sulfate. Distillation yields 18.0 g. (70%) of $n$-octanal, b.p. 83–85°/33 mm., $n_D^{20}$ 1.4217.

(+)-2-Butanol from *cis*-2-Butene (Preparation of Diisopino-campheylborane and Use in Asymmetric Synthesis).[17,57]  *A.* In a 500-ml. flask fitted with a condenser, a pressure-equalizing dropping funnel, and a thermometer are placed 75 ml. of $1M$ sodium borohydride (2.85 g.) in diglyme and 27.2 g. (0.2 mole) of (−)-$\alpha$-pinene, $[\alpha]_D^{20}$ −47.8°) in 100 ml. of diglyme. The flask is immersed in an ice bath and 12.6 ml. (14.2 g., 0.10 mole) of boron trifluoride etherate is added dropwise to the well-stirred reaction mixture. Stirring is continued for 4 hours at 0–5°. The diisopinocampheylborane separates as a thick white precipitate.

*B. cis*-2-Butene (8.5 ml., 6.1 g., 0.11 mole) is condensed at −78° and then introduced to the well-stirred diisopinocampheylborane. The reaction flask is equipped with a cold trap in order to minimize the loss of *cis*-2-butene. The reaction mixture is stirred for 2 hours at 0–5°, then allowed to warm to room temperature (2 hours). The excess hydride is decomposed by the addition of 10 ml. of water.

The organoborane is oxidized at 30–50° (water bath) by the addition of 32 ml. of $3N$ sodium hydroxide and 32 ml. of 30% hydrogen peroxide. The temperature is maintained at 45° for an additional hour.

The reaction mixture is extracted with three 100-ml. portions of ether. The combined extracts are washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether is removed and the product distilled. There is obtained 6.15 g. (83%) of 2-butanol; b.p. 98°/725 mm., $n_D^{20}$ 1.3970 $[\alpha]_D^{20}$ +11.6°.

The isopinocampheol formed in this reaction is obtained in 92% yield by distillation.

3-Ethyl-1-pentanol from 3-Ethyl-2-pentene (Preparation and Isomerization of an Alkylborane).[58]  *A.* To 50 ml. of diglyme

$$(C_2H_5)_2C=CHCH_3 \xrightarrow{BH_3} \left[ \begin{array}{c} CH_3 \\ | \\ (C_2H_5)_2CHCH- \end{array} \right]_2 BH \xrightarrow{Heat}$$

$$[(C_2H_5)_2CHCH_2CH_2-]_2BH \xrightarrow{[O]} (C_2H_5)_2CHCH_2CH_2OH$$
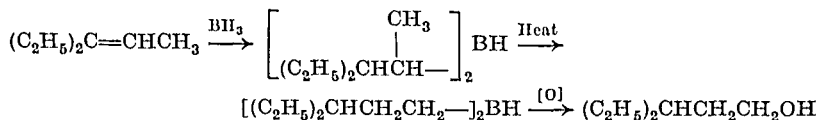
cooled in an ice bath is added 25 ml. of boron trifluoride etherate. The ether is removed by applying a vacuum of 5–10 mm. for 20 minutes while the flask is kept at 20–25°. The resulting boron trifluoride diglymate is

[57] H. C. Brown, N. R. Ayyangar, and G. Zweifel. Unpublished research.
[58] H. C. Brown and G. Zweifel. Unpublished research.

TABLE X

HYDROBORATION-OXIDATION OF OLEFINS

| No. of C Atoms | Olefin | Hydroborating Agent | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|---|
| C$_4$ | 1-Butene | $NaBH_4$-$BF_3$-Diglyme | 1-Butanol | 93 | 90–95* | 13 |
| | | | 2-Butanol | 7 | | |
| C$_5$ | 1-Pentene | $NaBH_4$-$BF_3$-Diglyme | 1-Pentanol | 94 | 90–95* | 1, 13 |
| | | | 2-Pentanol | 6 | | |
| | 2-Pentene (*cis* or *trans*) | $NaBH_4$-$BF_3$-Diglyme | 2-Pentanol | 51–55 | 90–95* | 13 |
| | | | 3-Pentanol | 45–49 | | |
| | 2-Methyl-1-butene | $NaBH_4$-$BF_3$-Diglyme | 2-Methyl-1-butanol | 99 | 90–95* | 13 |
| | | | 2-Methyl-2-butanol | 1 | | |
| | 2-Methyl-2-butene | $NaBH_4$-$BF_3$-Diglyme | 3-Methyl-2-butanol | 98 | 98* | 6, 13 |
| | | | 2-Methyl-2-butanol | 2 | | |
| | 3-Methyl-1-butene | $NaBH_4$-$BF_3$-Diglyme | 3-Methyl-1-butanol | 94 | 90–95* | 13 |
| | | | 3-Methyl-2-butanol | 6 | | |
| | Cyclopentene | $NaBH_4$-$AlCl_3$-Diglyme | Cyclopentanol | | 80 | 4 |
| | | $B_2H_6$-Triglyme | Cyclopentanol | | 90 | 1 |
| C$_6$ | 1-Hexene | $NaBH_4$-$AlCl_3$-Diglyme | 1-Hexanol | | 90 | 4 |
| | | $B_2H_6$-Diglyme | 1-Hexanol | | 87 | 1 |
| | | $NaBH_4$-$BF_3$-Diglyme | 1-Hexanol | 94 | 95 | 1, 13 |
| | | | 2-Hexanol | 6 | | |
| | | $[(CH_3)_2CHCH(CH_3){-}]_2$ BH·Diglyme | 1-Hexanol | 99 | 85–90* | 15 |
| | | | 2-Hexanol | 1 | | |
| | 2-Hexene (*cis* and *trans*) | $B_2H_6$-Diglyme | 2- and 3-Hexanol | 46–50 / 50–54 | 80 | 1 |
| | | $NaBH_4$-$BF_3$-Diglyme | 2-Hexanol | | 90 | 1, 13 |
| | | | 3-Hexanol | | | |
| | *cis*-3-Hexene | $NaBH_4$-$BF_3$-Diglyme | 3-Hexanol | 100 | 90–95* | 13 |
| | 3,3-Dimethyl-1-butene | $NaBH_4$-$AlCl_3$-Diglyme | 3,3-Dimethyl-1-butanol | | 67 | 4 |
| | | $B_2H_6$-Triglyme | 3,3-Dimethyl-1-butanol | | 62 | 1 |
| | | $NaBH_4$-$BF_3$-Diglyme | 3,3-Dimethyl-1-butanol | 94 | | 1, 13 |
| | | | 3,3-Dimethyl-2-butanol | 6 | | |

|  | Olefin | Reagent | Product | % | Yield | Ref. |
|---|---|---|---|---|---|---|
| $C_7$ | 4 Methyl 1 pentene 2 Methyl 2 pentene | NaBH₄ BF₃ THF NaBH₄ BF₃ Diglyme | 4 Methyl 1 pentanol 4 Methyl 2 pentanol 2 Methyl 2 pentanol | 57 43 | 80 | 49 13 |
|  | cis 4 Methyl 2 pentene | [(CH₂)₂CHCH=]₂ BH | 4 Methyl 2 pentanol 2 Methyl 3 pentanol | 95 5 | 85–90* | 15 |
|  |  | [(CH₂)₂CHCH=]₂ BH | 4 Methyl 2 pentanol 2 Methyl 3 pentanol | 97 3 | 85–90* | 15 |
|  | Cyclohexene 1-Methylcyclopentene | LiAlH₄ BF₃ diethyl ether B₂H₆ THF | Cyclohexanol trans 2 Methylcyclopentanol | 93 7 | 80 96 | 53 11 13 |
|  | trans 4,4 Dimethyl 2 pentene | NaBH₄ BF₃ Diglyme | 4,4 Dimethyl 1 pentanol 4,4 Dimethyl 2 pentanol 2,2 Dimethyl 3 pentanol | 52 88 | 85–90* | 13 |
|  | 3 Ethyl 1 pentene | NaBH₄ BF₃ Diglyme | 3 Ethyl 1 pentanol 3 Ethyl 2 pentanol | 90 10 | 85 | 23 |
|  | 3 Ethyl 2 pentene 1 Methylcyclohexene | NaBH₄ BF₃ Diglyme B₂H₆ Diglyme | 3 Ethyl 2 pentanol trans 2 Methylcyclohexanol | 83 85 | 83 85 | 23 11 |
|  | 3 Methylcyclohexene | B₂H₆ THF | 2 Methylcyclohexanol (cis and trans) 3 Methylcyclohexanol | 48 52 | 80 | 11 |
| $C_8$ | 1,2 Dimethylcyclopentene Norbornene | B₂H₆ THF LiAlH₄ HCl THF | cis 2 Dimethylcyclopentanol) exo Norborneol | 99 | 75–85 70 | 11 49 |
|  | 1-Octene 2,4,4 Trimethyl 1 pentene | NaBH₄ BF₃ diethyl ether LiBH₄ THF NaBH₄ BF₃ Diglyme | 1 Octanol 2,4,4 Trimethyl 1 pentanol 2,4,4 Trimethyl 3 pentanol | 99 1 | 80 80 81 | 53 49 13 |
|  | 2,4,4 Trimethyl 2 pentene | NaBH₄ BF₃ Diglyme | 2,4,4 Trimethyl 2 pentanol 2,4,4 Trimethyl 3 pentanol | 2 98 | 79* | 6,13 |

Note. References 59 to 70 are on p. 54.
* The yield was determined by vapor phase chromatography.

TABLE X—*Continued*

HYDROBORATION-OXIDATION OF OLEFINS

| No. of C Atoms | Olefin | Hydroborating Agent | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|---|
| C₈ (*contd.*) | 1,2-Dimethylcyclo-hexene | B₂H₆-THF | cis-1,2-Dimethylcyclo-hexanol | | 82 | 11 |
| | 3,3-Dimethylcyclo-hexene | B₂H₆-THF | 2,2-Dimethylcyclohexanol<br>3,3-Dimethylcyclohexanol | 50<br>50 | — | 11 |
| | | $\left[ \text{(CH}_3\text{)}_2\text{CHCH} \xrightarrow{\underset{|}{\text{CH}_3}} \right]_2 \text{BH}$ | 2,2-Dimethylcyclohexanol<br>3,3-Dimethylcyclohexanol | 40<br>60 | — | 11 |
| | Styrene | NaBH₄-AlCl₃-Diglyme<br>LiBH₄-BF₃-diethyl ether | 2-Phenyl-1-ethanol<br>1-Phenyl-1-ethanol<br>2-Phenyl-1-ethanol<br>1-Phenyl-1-ethanol | 20<br>80<br>18<br>82 | 81<br>91* | 4<br>13 |
| | | B₂H₆-Diglyme | 2-Phenyl-1-ethanol<br>1-Phenyl-1-ethanol | 20<br>80 | 95* | 13 |
| | | NaBH₄-BF₃-Diglyme | 2-Phenyl-1-ethanol<br>1-Phenyl-1-ethanol | | 94* | 13 |
| C₉ | α-Methylstyrene<br>p-Methylstyrene | NaBH₄-BF₃-Diglyme<br>NaBH₄-BF₃-Diglyme | 2-Phenyl-1-propanol<br>1-p-Tolyl-1-ethanol<br>2-p-Tolyl-1-ethanol | 100<br>18<br>82 | 92<br>— | 1, 13<br>13 |
| | Allylbenzene | NaBH₄-BF₃-Diglyme | 1-Phenyl-2-propanol<br>3-Phenyl-1-propanol | 10<br>90 | — | 13 |
| | trans-1-Phenylpropene | NaBH₄-BF₃-Diglyme | 1-Phenyl-1-propanol<br>1-Phenyl-2-propanol | 85<br>15 | — | 13 |
| C₁₀ | 1-Decene | NaBH₄-BF₃-Diglyme<br>B₂H₆† | 1-Decanol<br>1-Decanol | | 85<br>92 | 1<br>1 |
| | 1,1-Di-t-butylethylene<br>1,2-Di-t-butylethylene<br>1-Phenylcyclobutene | B₂H₆-Diglyme<br>B₂H₆-THF | [(CH₃)₃C]₂CHCH₂OH<br>(CH₃)₃CCHOHCH₂C(CH₃)₃<br>2-Phenylcyclobutanol | | 82<br>82 | 60<br>12<br>69 |

| | Reagent | | Yield | |
|---|---|---|---|---|
| CH₂ (structure) | NaBH₄, BF₃, Diglyme | CH₂OH / —H (structure) | 81 | 11 |
| CH₃ (structure) | B₂H₆, THF | CH₃ —M—OH (structure) | 89 | 11 |
| CH₂ (structure) | B₂H₆, THF-diethyl ether | H CH₂OH (structure) *endo* | 77 | 61 |
| (structure) | B₂H₆, Diglyme | HO (structure) *exo* | 28 | 62 |
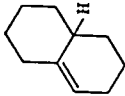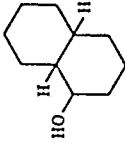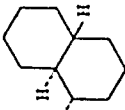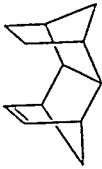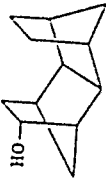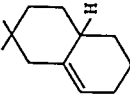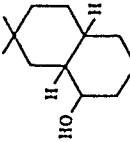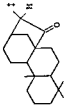
*Note:* References 69 to 70 are on p. 54.

* The yield was determined by vapor-phase chromatography.

† The conditions for hydroboration were not reported.

## TABLE X—*Continued*

### HYDROBORATION-OXIDATION OF OLEFINS

| No. of C Atoms | Olefin | Hydroborating Agent | Oxidation Product(s) | Isomer Distribu- tion, % | Yield, % | References |
|---|---|---|---|---|---|---|
| C₁₁ |  | LiAlH₄·BF₃·diethyl ether |  | | — | 53 |
| C₁₂ |  | B₂H₆† |  | | — | 20 |
| C₁₃ |  | LiAlH₄·BF₃·diethyl ether |  | | — | 53 |

| | | | | | |
|---|---|---|---|---|---|
| C$_{14}$ | 1,1 Diphenylethylene  | NaBH$_4$, AlCl$_3$, Diglyme | 2,2 Diphenylethanol | 71 | 4 |
| |  | NaBH$_4$, BF$_3$-Diglyme |  | 35 | 63 |
| C$_{20}$ |  | LiAlH$_4$, BF$_3$, diethyl ether |  | — | 64 |

*Note:* References 59 to 70 are on p 54.

† The conditions for hydroboration were not reported.

‡ The alcohol was oxidized directly to the ketone.

TABLE XI

HYDROBORATION-OXIDATION OF STEROIDS

| Name | Hydroborating Agent | Oxidation Product(s) | Yield, % | Reference |
|---|---|---|---|---|
| Cholesterol | $B_2H_6$* | Cholestane-3β,6α-diol | 45 | 9 |
| | LiAlH₄·BF₃·diethyl ether | Coprostane-3β,6β-diol | 70 | 52 |
| | | Cholestane-3β,6α-diol diacetate | | |
| | | Coprostane-3β,6β-diol diacetate | 10–20 | |
| 1-Cholestene | LiAlH₄·BF₃·diethyl ether | Cholestan-1α-ol | 35 —— | 16 |
| | | Cholestan-2α-ol | 40 | |
| | $\left[ (CH_3)_2CHCH(\overset{CH_3}{\mid})\!\!-\!\! \right]_2 BH$ | Cholestan-2α-ol | 75 | 16 |
| 2-Cholestene | LiAlH₄·BF₃·diethyl ether or $B_2H_6$·THF | Cholestan-2α-ol | 35 | 16 |
| | | Cholestan-3α-ol | 45 | |
| | $\left[ (CH_3)_2CHCH(\overset{CH_3}{\mid})\!\!-\!\! \right]_2 BH$ | Cholestan-2α-ol | 35 | 16 |
| | | Cholestan-3α-ol | 45 | |
| 3-Cholestene | LiAlH₄·BF₃·diethyl ether | Cholestan-3α-ol | 40 | 16 |
| | | Cholestan-4α-ol | 45 | |
| | $\left[ (CH_3)_2CHCH(\overset{CH_3}{\mid})\!\!-\!\! \right]_2 BH$ | Cholestan-3α-ol | 45 | 16 |
| | | Cholestan-4α-ol | 35 | |

| Substrate | Reagent | Product | | |
|---|---|---|---|---|
| 4 Cholestane | LiAlH₄/BF₃-diethyl ether | Cholestan-4α-ol | 60 | 52 |
| 5 Cholestene | LiAlH₄/BF₃-diethyl ether | Cholestan-6α-ol | 75 | 52 |
| Andros-9(11)-ene | LiAlH₄/BF₃-diethyl ether | Androstan-9α-ol | 90 | 10 |
| | | Androstan-11α-ol | 55 | 10 |
| Δ¹⁶-Androstano-3β,17-diol diacetate | B₂H₆/THF (Diglyme) | Androstano-3β,16α,17β triol-3-methyl ether | 44 | 35 |
| Δ¹⁴,¹⁶-Estratetraeno-3,17-diol-3-methyl ether 17-acetate | B₂H₆/THF (Diglyme) | Estriol 3-methyl ether | 50 | 65 |
| Δ¹,⁴,¹⁶-Estratetraene 17-acetate | B₂H₆, THF (Diglyme) | Estriol | | 65 |
| 3,20-Bis(ethylenedioxy)-5α pregn-9(11)-ene | B₂H₆, THF (Diglyme) | 11-α-Hydroxy-5α-pregnane-3,20-dione | 40 | 10 |
| 3,20-Biscyclohexylenedioxy-5β-pregn-9(11)-ene | B₂H₆, THF | No reaction | 55 | |
| 5α-25D-Spirost-9(11)-en-3β-ol acetate | B₂H₆, THF | 5α-25D-Spirostane-3β,11α-diol diacetate | 60 | 9 |
| | | 5α-22a-Spirostane-3β,11α-diol | 40 | 10 |
| 5α-22a-Spirost-1[(11)]-en-3β-ol acetate | B₂H₆, THF | 5α-22a-Spirostane-3β,12α-diol | 40 | 18 |
| Test-9(11)-ene | LiAlH₄/BF₃-Diglyme | No reaction | | 10 |
| | B₂H₆-THF | No reaction | | 10 |

Note: References 59 to 70 are on p. 54.

* The conditions for hydroboration were not reported.

## TABLE XII
### ASYMMETRIC SYNTHESES OF ALCOHOLS

| Olefin | Hydroborating Agent | Optically Active Alcohol (Rotation, $[\alpha]_D^{20}$) | Optical Purity, % | Yield, % | References |
|---|---|---|---|---|---|
| cis-2-Butene | Diisopinocampheylborane from (+)-α-pinene | 2-Butanol (−11.8°) | 87 | 90 | 17, 18 |
| | Diisopinocampheylborane from (−)-α-pinene | 2-Butanol (+11.6°) | 86 | 83 | 18 |
| cis-3-Hexene | Diisopinocampheylborane from (+)-α-pinene | 3-Hexanol (−6.5°) | 91 | 81 | 17 |
| cis-4-Methyl-2-pentene | Diisopinocampheylborane from (+)-α-pinene | 4-Methyl-2-pentanol (+16.0°) | 76 | — | 18 |
| Norbornene | Diisopinocampheylborane from (−)-α-pinene | exo-Norborneol (−2.0°) | 70 | 62 | 17, 18 |
| | Diisopinocampheylborane from (−)-α-pinene | exo-Norborneol (+1.95°) | 70 | 56 | 18 |

*Note:* References 59 to 70 are on p. 54.

TABLE XIII

HYDROBORATION-OXIDATION OF OLEFINS CONTAINING OTHER FUNCTIONAL GROUPS

| Olefin | Hydroborating Agent | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|
| $H_2C$=CHCH$_2$Cl | [(CH$_3$)$_2$CHCH—]$_3$ BH THF | HOCH$_2$CH$_2$CH$_2$Cl | | 77* | 68 |
| $H_2C$=CHCH$_2$CH$_2$Cl | [(CH$_3$)$_2$CHCH—]$_3$ BH THF | HOCH$_2$CH$_2$CH$_2$CH$_2$Cl | | 88* | 66 |
| (CH$_3$)$_2$SCH=CH$_2$ | NaBH$_4$, AlCl$_3$, Diglyme | (CH$_3$)$_2$SCH$_2$CH$_2$CH$_2$OH / (CH$_3$)$_2$SCH(OH)CH$_3$ | 63 / 37 | 75 | 14 |
| [cyclic structure, S O$_2$] | B$_2$H$_6$ THF | [cyclic structure, HO—, S O$_2$] | | 63 | 67 |
| $H_2C$=CHCH$_2$CO$_2$C$_2$H$_5$ | [(CH$_3$)$_2$CHCH—]$_3$ BH·THF | HOCH$_2$CH$_2$CH$_2$CO$_2$C$_2$H$_5$ | | 76 | 66 |
| $H_2C$=CHCH$_2$CH$_2$CO$_2$C$_2$H$_5$ | [(CH$_3$)$_2$CHCH—]$_3$ BH Diglyme | HOCH$_2$CH$_2$CH$_2$CH$_2$CO$_2$C$_2$H$_5$ | | 78 | 66 |
| p Chlorostyrene | NaBH$_4$, BF$_3$ Diglyme | 1 p Chlorophenyl 2 ethanol / 1 p Chlorophenyl 1 ethanol | 65 / 35 | — | 13 |
| p Methoxystyrene | NaBH$_4$, BF$_3$ Diglyme | 1 p Anisyl 2 ethanol / 1 p Anisyl 1 ethanol | 91 / 9 | — | 13 |
| | [(CH$_3$)$_2$CHCH—]$_3$ BH·THF | 1 p Anisyl 2 ethanol / 1 p Anisyl 1 ethanol | 98 / 2 | 80 | 15 |
| 1,2 O Isopropylidene-4 vinyl α D xylotetofuranose | B$_2$H$_6$† | 5 Decyl 1,2 O isopropylidene-α D xylohexofuranose | | — | 68 |

Note: References 53 to 70 are on p. 54.
* The yield was determined by vapor phase chromatography.
† The conditions for hydroboration were not reported.

TABLE XIII—*Continued*

| Olefin | Hydroborating Agent | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|
| Anethole | $B_2H_6$·diethyl ether | 1-p-Anisyl-1-propanol<br>1-p-Anisyl-2-propanol | 75<br>25 | 66 | 33 |
| $trans$-$p$-$CH_3OC_6H_4C(CH_3)$=$CHCH_3$ | $B_2H_6$·diethyl ether |  | | 72 | 33 |
| $cis$-$p$-$CH_3OC_6H_4C(CH_3)$=$CHCH_3$ | $B_2H_6$·diethyl ether |  | | 77 | 33 |
|  | $B_2H_6$·diethyl ether |  | | — | 19, 20 |
| $H_2C$=$CH(CH_2)_8CO_2C_2H_5$ | $B_2H_6$-THF | $HOCH_2CH_2(CH_2)_8CO_2C_2H_5$ | | 71 | 61, 66 |
| | $\left[ (CH_3)_2CHCH{-}CH_3 \right]_2$ BH-THF | $HOCH_2CH_2(CH_2)_8CO_2C_2H_5$ | | 81 | 66 |
| $H_2C$=$CH(CH_2)_8CO_2H$ | $\left[ (CH_3)_2CHCH{-}CH_3 \right]_2$ BH-THF | $HOCH_2CH_2(CH_2)_8CO_2H$ | | 82 | 38 |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2CH_3$ | $B_2H_6$-Diglyme | $CH_3(CH_2)_7CH_2CHOH$·$(CH_2)_7CO_2CH_3$<br>$CH_3(CH_2)_7CHOHCH_2$·$(CH_2)_7CO_2CH_3$ | 50<br>50 | — | 39 |

*Note:* References 59 to 70 are on p. 54.

TABLE XIV

HYDROBORATION-OXIDATION OF DIENES

| Diene | Monohydroboration, Reagent | Dihydroboration, Reagent | Oxidation Products(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|---|
| 1,3 Butadiene | $B_2H_6$, THF | | 1,3-Butanediol / 1,4-Butanediol | 20 / 80 | 74 | 29 |
| | | $\left[(CH_3)_2CHCH—\right]_2$ / BH·THF | 1,3-Butanediol / 1,4-Butanediol | 10 / 90 | 78 | 34 |
| 2 Methyl 1,3 butadiene | $B_2H_6$, THF | | 2 Methyl 1,3-butanediol / 2 Methyl 1,4 butanediol | 13 / 87 | 60 | 29 |
| 1,3 Pentadiene (cis and trans) | $\left[(CH_3)_2CHCH—\right]_2$ | BH·THF | 3-Pentene-1-ol (cis and trans) | | 74 | 34 |
| 1,4 Pentadiene | $B_2H_6$-THF | | 1,4 Pentanediol / 1,5 Pentanediol | 62 / 38 | — | 29 |
| | | $\left[(CH_3)_2CHCH—\right]_2$ / BH·THF | 1,4 Pentanediol / 1,5 Pentanediol | 15 / 85 | — | 34 |
| 2,3 Dimethyl-1,3 butadiene | $B_2H_6$-THF | | 2,3 Dimethyl 1,4-butanediol | | 66 | 29 |
| | $B_2H_6$-Diglyme | | 1,5 Hexanediol / 1,6 Hexanediol | 13 / 87 | 78 | 31 |
| 1,4 Hexadiene | $B_2H_6$-THF | | 5 Hexen 1 ol | | 28 | 29 |
| 1,5 Hexadiene | $B_2H_6$-THF | | 5 Hexen-1-ol | | 51 | 34 |
| | | $\left[(CH_3)_2CHCH—\right]_2$ | 1,6 Hexanediol | | 79 | 29 |
| | | BH·THF | 1,5 Hexanediol / 1,6 Hexanediol / 2,3 Hexanediol(?) / 1,4 Hexanediol | 22 / 69 / 9 | 72 | 34 |

TABLE XIV—*Continued*

HYDROBORATION-OXIDATION OF DIENES

| Diene | Monohydroboration, Reagent | Dihydroboration, Reagent | Oxidation Product(s) | Isomer Distribution, % | Yield, % | Reference |
|---|---|---|---|---|---|---|
| 2-Methyl-1,5-hexadiene | $\left[(CH_3)_2CHCH-\right]_3$ BH·THF (with CH₃) | | $CH_2{=}C(CH_3)CH_2\text{-}CH_2CH_2CH_2OH$ | | 68 | 34 |
| Cyclopentadiene | $B_2H_6$·diethyl ether | | 3-Cyclopentene-1-ol | | 30 | 33 |
| | | $B_2H_6$·diethyl ether | trans-1,3-Cyclo-pentanediol | | 41 | 31, 32 |
| 1,3-Cyclohexadiene | $B_2H_6$·THF | | 2-Cyclohexen-1-ol 3-Cyclohexen-1-ol | 60–65 35–40 | — | 29 |
| | $\left[(CH_3)_2CHCH-\right]_3$ BH·THF (with CH₃) | | 2-Cyclohexen-1-ol 3-Cyclohexen-1-ol | 90 10 | 70 | 34 |
| 1,4-Cyclohexadiene | $\left[(CH_3)_2CHCH-\right]_2$ BH·THF (with CH₃) | | 3-Cyclohexen-1-ol | | 75 | 34 |
| Bicycloheptadiene | $LiBH_4$·$BF_3$·diethyl ether | | exo-Dehydro-norborneol endo-Dehydro-norborneol | 88 12 | 45 | 29 |
| | $B_2H_6$·THF | | exo-Dehydro-norborneol endo-Dehydro-norborneol | 87 13 | 39* | 29 |
| | $\left[(CH_3)_2CHCH-\right]_2$ BH·THF (with CH₃) | | exo-Dehydro-norborneol endo-Dehydro-norborneol | 87 13 | 45* | 34 |
| | | $B_2H_6$·THF | Mixture of diols (?) | | 64 | 29 |

| | | |
|---|---|---|
| 72 | $[CH_3]_2CHCH{-}]_2$ CH₃ BH-Diglyme | CH₂CH₂OH | 15 |
| 79 | $[CH_3]_2CHCH{-}]_2$ CH₃ BH-Diglyme | CH₂OH | 15 |
| 85 | $[(CH_3)_2CHCH{-}]_2$ CH₃ BH·THF | Mixture of diols | 34 |
| — | $(CH_3)_2C{=}CHCH_2]_2$ C=CH·CH₂CH₂OH | | 35 |
| — | D₂N·THF | HOCH₂ / HO—H | 69 |
| 3.5 | $[CH_3]_2CHCH{-}]_2$ CH₃ BH THF | | 3.5 |

CH=CH₂

1,5-Cyclooctadiene

$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CH_2CH{=}CH_2$

Note: References 68 to 70 are on p. 54
* The yield was determined by vapor phase chromatography.

TABLE XV

MONOHYDROBORATION-OXIDATION OF ACETYLENES

| Acetylene | Hydroborating Agent | Oxidation Product | Yield, % | Reference |
|---|---|---|---|---|
| 1-Butyne | $t\text{-}C_4H_9\overset{-}{B}H_2\overset{+}{N}(CH_3)_3$ | n-Butyraldehyde* | — | 36 |
| 1-Hexyne | $\left[(CH_3)_2CHCH\overset{CH_3}{\underset{\vert}{\vert}}\right]_2 BH\cdot Diglyme$ | n-Hexanal* | — | 2 |
| 3-Hexyne | $\left[(CH_3)_2CHCH\overset{CH_3}{\underset{\vert}{\vert}}\right]_2 BH\cdot Diglyme$ | 3-Hexanone | 62 | 2 |
| 1-Octyne | $\left[(CH_3)_2CHCH\overset{CH_3}{\underset{\vert}{\vert}}\right]_2 BH\cdot Diglyme$ | n-Octanal | 70 | 2 |

Note: References 59 to 70 are on p. 54.

* The product was identified as the 2,4-dinitrophenylhydrazone.
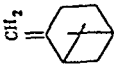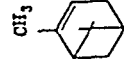
TABLE XVI

ISOMERIZATION-OXIDATION OF ORGANOBORANES

| Unsaturated Compound | Hydroborating Agent | Isomerization Time, hr. | Isomerization Temp, °C. | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|---|---|
| 2-Pentene | NaBH₄, BF₃·Diglyme | 1 | 160 | 1 Pentanol / 2 Pentanol / 3 Pentanol | 85 / 14 / 1 | 82 | 22, 23 |
| 1,3-Pentadiene | B₂H₆* | 6 | 160–175 | 1,5-Pentanediol | — | — | 31 |
| 2-Methyl-1 butene | NaBH₄, BF₃·Diglyme | 4 | 160 | 3 Methyl 1 butanol / 2 Methyl 1 butanol / 2 Methyl 2 butanol | 43 / 54 / 2 | 83 | 23 |
| 2-Methyl 2 butene | NaBH₄, BF₃·Diglyme | 4 | 160 | 3 Methyl 1 butanol / 2 Methyl 1 butanol / 2 Methyl 2 butanol | 58 / 40 / 2 | — | 23 |
| 3 Methyl 1-butene | NaBH₄, BF₃·Diglyme | 1 | 160 | 3 Methyl 1 butanol / 2 Methyl 1 butanol | 59 / 30 | — | 23 |
| 2 Hexene | NaBH₄, BF₃·Diglyme | 1 | 160 | 1 Hexanol / 2 Hexanol / 3 Hexanol | 91 / 6 / 3 | 75 | 22, 23 |
| cis 3-Hexene | NaBH₄, BF₃·Diglyme | 1 | 160 | 1 Hexanol / 2 Hexanol / 3 Hexanol | 90 / 6 / 4 | — | 23 |
| 1,4-Hexadiene | B₂H₆* | 6 | 160–175 | 1,6 Hexanediol / 1,5 Hexanediol | 69 / 30 | 82 | 31 |
| 1,5 Hexadiene | B₂H₆* | 6 | 100–115 | 1,6 Hexanediol | 70 / 30 | 78 | 31 |
| 4,4-Dimethyl 2 pentene | NaBH₄, BF₃·Diglyme | 1 | 160 | 4,4-Dimethyl 1 pentanol / 4,4 Dimethyl 2 pentanol / 2,2 Dimethyl 3 pentanol | 96 / 2 / 2 | — | 23 |

* The conditions for hydroboration were not reported.

## TABLE XVI—Continued

| Unsaturated Compound | Hydroborating Agent | Isomerization Time, hr. | Isomerization Temp., °C, | Oxidation Product(s) | Isomer Distribution, % | Yield, % | References |
|---|---|---|---|---|---|---|---|
| 3-Ethyl-2-pentene | NaBH₄·BF₃·Diglyme | 2 | 160 | 3-Ethyl-1-pentanol | | 88 | 23 |
|  | NaBH₄·BF₃·Diglyme | 4 | 160 |  CH₂OH | | — | 23 |
| 2,4,4-Trimethyl-2-pentene | NaBH₄·BF₃·Diglyme | 1 | 160 | 2,4,4-Trimethyl-1-pentanol<br>2,4,4-Trimethyl-2-pentanol<br>2,4,4-Trimethyl-3-pentanol | 97<br>1<br>2 | — | 23 |
| C₆H₅CH₂CH=CHCH₃ | NaBH₄·BF₃·Diglyme | 1 | 160 | C₆H₅CH₂CH₂CH₂OH<br>C₆H₅CH₂CH₂CHOHCH₃<br>C₆H₅CHOHCH₂CH₃ | 76<br>10<br>14 | — | 23 |
| Decenes (mixed) | NaBH₄·BF₃·Diglyme | 4 | 160 | 1-Decanol | | 70–80 | 22 |
|  CH₂ | NaBH₄·BF₃·Diglyme | 4 | 160 |  H CH₂OH | | 80 | 24, 25 |
|  CH₃ | NaBH₄·BF₃·Diglyme | 4 | 160 |  H CH₂OH | | 80 | 24, 25 |
| 3-Carene | B₂H₆* | 1 | 150 | 10-Hydroxycarane | | — | 70 |

*Note:* References 59 to 70 are on p. 54.
* The conditions for hydroboration were not reported.

TABLE XVII

CHROMIC ACID OXIDATION OF ORGANOBORANES

| Olefin | Hydroborating Agent | Oxidation Product | Yield, % | Reference |
|---|---|---|---|---|
| Geraniene | $NaBH_4–AlCl_3$–Diglyme | 3,$\beta$-Dimethyl,laminocrotonin 6 one | – | 46 |
| Cyclohexene | $LiBH_4,BF_3$–diethyl ether | Cyclohexanone | 60–63 | 47 |
| 1-Methylcyclopentene | $LiBH_4,BF_3$–diethyl ether | 2-Methylcyclopentanone | 83 | 47 |
| 1-Methylcyclohexene | $LiBH_4,BF_3$–diethyl ether | 2-Methylcyclohexanone | 87 | 47 |
| 1-Phenylcyclohexene | $LiBH_4,BF_3$–diethyl ether | 2-Phenylcyclohexanone | 63 | 47 |
| $\alpha$-Pinene | $LiBH_4,BF_3$–diethyl ether | Isopinocamphone | 72 | 47 |

## REFERENCES FOR TABLES X–XVII

[59] Beard and Burger, *J. Org. Chem.*, **26**, 2335 (1961).

[60] Newman, Arkell, and Fukunago, *J. Am. Chem. Soc*, **82**, 2498 (1960).

[61] Dulou and Chrétien-Bessière, *Bull. Soc. Chim. France*, **1959**, 1362.

[62] Cristol, Seifert, and Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).

[63] Dauben, Weinstein, Lim, and Anderson, *Tetrahedron*, **15**, 217 (1961).

[64] Henderson and Hoges, *Tetrahedron*, **11**, 226 (1960).

[65] Alvarez and Arreguin, *Chem. & Ind. (London)*, **1960**, 720.

[66] H. C. Brown and K. Keblys. Unpublished research.

[67] Krug and Boswell, *J. Org. Chem.*, **27**, 95 (1962).

[68] Wolfrom and Whiteley, *Am. Chem. Soc. Meeting, Abstr.*, April 1960, 2D.

[69] Cornforth, *J. Pure and Appl. Chem.*, **2**, 607 (1961).

[70] Arlt, Sheers, and Chamberlain, *Chem. & Ind. (London)*, **1961**, 1409.

# CHAPTER 2

# HALOCYCLOPROPANES FROM HALOCARBENES

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## CONTENTS

## INTRODUCTION

This chapter reviews methods for the generation of halocarbenes and the reactions of the latter with unsaturated substrates. Chemical transformations of the derived halocyclopropanes are discussed in sufficient detail to demonstrate the synthetic utility of this class. A number of review articles have appeared which discuss carbenes in general and which include some of the halocarbene reactions.[1-4a] Other chemical reactions that probably proceed by way of dihalocarbenes, such as the Reimer-Tiemann reaction[5] and the Hofmann isonitrile synthesis,[6,7] are not included in this review.

The formation of dihalocyclopropanes from dihalocarbenes was first accomplished in 1954 by Doering and Hoffmann,[8] who used chloroform and
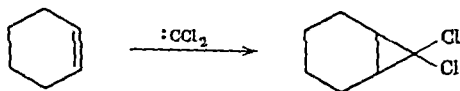


potassium t-butoxide to generate the dichlorocarbene. Since that time, a variety of other methods have been developed for the generation of halocarbenes. They are illustrated by the following equations.

[1] Knunyants, Gambaryan, and Rokhlin, Uspekhi Khim., 27, 1361 (1958) [C.A., 53, 5107 (1959)].

[2] Kirmse, Angew Chem., 71, 537 (1959).

[3] Vogel, Angew Chem., 72, 4 (1960).

[4] Kirmse, Angew Chem., 73, 161 (1961).

[4a] Leitlich, Oesterr. Chemiker Z., 61, 164 (1960).

[5] Wynberg, Chem. Revs., 60, 169 (1960).

[6] Smith and Kalenda, J. Org. Chem., 23, 1599 (1958).

[7] Frankel, Feuer, and Bank, Tetrahedron Letters, 7, 5 (1959).

[8] Doering and Hoffmann, J. Am. Chem. Soc., 76, 6162 (1954).

$$CHCl_3 + KOC_4H_9\text{-}t \rightarrow :CCl_2 + KCl + HOC_4H_9\text{-}t \qquad \text{(Ref. 8)}$$

$$BrCCl_3 + LiC_4H_9\text{-}n \rightarrow :CCl_2 + LiCl + n\text{-}C_4H_9Br \qquad \text{(Ref. 9)}$$

$$Cl_3CH_3 + LiC_4H_9\text{-}n \rightarrow :CHCl + LiCl + n\text{-}C_4H_{10} \qquad \text{(Ref. 10)}$$

$$Cl_3CCOOCl_3 + 2RO^\ominus \rightarrow 2:CCl_2 + (RO)_2CO + 2Cl^\ominus \qquad \text{(Ref. 11)}$$

$$Cl_3CCO_2Na \rightarrow CCl_2 + NaCl + CO_2 \qquad \text{(Ref. 12)}$$

$$Cl_3CCO_2R + RO^\ominus \rightarrow :CCl_2 + (RO)_2CO + Cl^\ominus \qquad \text{(Ref. 13)}$$

$$C_6H_5HgCCl_3 \rightarrow :CCl_2 + C_6H_5HgCl \qquad \text{(Ref. 13a)}$$
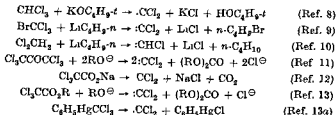
## STRUCTURE AND MECHANISM

The halocarbenes are not isolated as such, but the *weight of present evidence* is that they are in fact low-energy intermediates along the path from the reactants to the products. The postulated structure of the dichlorocarbene intermediate is that shown.[14,15] The trigonal carbon



atom is considered to have two covalent bonds joining it to the halogen atoms, a pair of electrons having antiparallel spins (singlet state) and an unoccupied *p*-orbital. It is probable that considerable stabilization of this structure is the consequence of overlap of the unshared *p*-electrons of the halogen atoms with the vacant *p*-orbital.[14,16–19] Overlap from fluorine is more effective than from chlorine,[20] and as a result difluorocarbene appears to be substantially less reactive than dichlorocarbene.[19,21–24]

⁸ Miller and Kim, *J. Am. Chem. Soc.*, **81**, 6008 (1959).
⁹ Closs and Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).
¹⁰ Grant and Cason, *J. Org. Chem.*, **25**, 1433 (1960)
¹¹ W W. Wagner, *Proc. Chem. Soc.*, 1959, 229
¹² Parham and Schweizer, *J. Org Chem.*, **24**, 1733 (1959)
¹²ᵃ Seyferth, Burlitch, and Heeren, *J Org. Chem*, **27**, 1491 (1962).
¹³ Skell and Garner, *J. Am. Chem Soc.*, **78**, 5430 (1956).
¹⁴ Skell and Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); **79**, 6577 (1957)
¹⁵ Hine and Ehrenson, *J. Am. Chem. Soc.*, **80**, 824 (1958).
¹⁶ Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).
¹⁷ Skell and Etter, *Chem. & Ind* (*London*), 1958, 624.
¹⁸ Venkateswarlu, *Phys Rev.*, **77**, 676 (1950).
¹⁹ Hine and Rosscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).
²⁰ Laird, Andrews, and Barrow, *Trans Faraday Soc*, **46**, 803 (1950).
²¹ Margrave and Wieland, *J Chem. Phys*, **21**, 1552 (1953).
²² Duchesne and Burnelle, *J Chem. Phys.*, **21**, 2005 (1953)
²³ Franzen, *Chem Ber*, **95**, 1964 (1962).

The addition of dihalocarbenes to olefins has been shown by Skell[14] and by Doering[25] to be a stereospecific *cis* addition. (See also pp. 65–66.) This work supports the view that the addition is a concerted three-center process. To be stereospecific, a stepwise process leading to a charge-separated intermediate would require that this intermediate collapse to
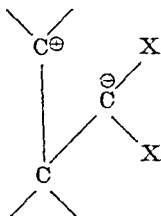


the cyclopropane faster than rotation could occur about a C—C single bond. The stereospecific character of the reaction also supports the view that dihalocarbenes exist in the singlet ground state.[26-28]

### PREPARATION OF HALOCARBENES

**Alkoxide-Haloform Reactions.** In 1854, Williamson studied the reactions of chloroform with ethanolic sodium ethoxide and isolated triethyl orthoformate as the principal product.[29] This study was followed by a number of others that dealt with the reactions of haloforms with alkoxides and alcohols[30,31] and with heterocyclic nitrogen compounds.[32-35] In 1862, Geuther[36] postulated a dichlorocarbon intermediate, a concept generally accepted by chemists.[37-43]

[25] Doering and LaFlamme, *J. Am. Chem. Soc.*, 78, 5447 (1956).
[26] Woodworth and Skell, *J. Am. Chem. Soc.*, 81, 3383 (1959).
[27] Etter, Skovronek, and Skell, *J. Am. Chem. Soc.*, 81, 1008 (1959).
[28] Parham and Hasek, *J. Am. Chem. Soc.*, 76, 935 (1954).
[29] Williamson, *Proc. Roy. Soc. (London)*, 7, 135 (1854).
[30] Bassett, *Ann.*, 132, 54 (1864).
[31] Gorboff and Kessler, *J. Prakt. Chem.*, [2] 41, 224 (1890).
[32] Ciamician, *Ber.*, 37, 4231 (1904).
[33] Magnanini, *Ber.*, 20, 2608, (1887); *Gazz. Chim. Ital.*, 17, 246 (1887).
[34] Zanetti and Levi, *Gazz. Chim. Ital.*, 24 [II], 111 (1894).
[35] Bocchi, *Gazz. Chim. Ital.*, 30 [I], 89 (1900).
[36] Geuther, *Ann.*, 123, 121 (1862).
[37] Ciamician and Dennstedt, *Ber.*, 14, 1153 (1881).
[38] Urbain, *Bull. Soc. Chim. France*, [4] 51, 853 (1932).
[39] Tchakirian, *Bull. Soc. Chim. France*, [4] 51, 846 (1932).
[40] Urbain, *Bull. Soc. Chim. France*, [4] 53, 637 (1933).
[41] Messler, *Monatsh. Chem.*, 29, 573 (1908).
[42] Thiele and Dent, *Ann.*, 302, 273 (1898).
[43] Nef, *J. Am. Chem. Soc.*, 30, 645 (1905).

Interest in this reaction was renewed in 1950 when Hine published the first of a series of papers in which he elucidated the mechanism of haloform-base reactions.[16][17,44–47] Hine postulated an initial fast attack of base on chloroform to give the trichloromethyl anion and the conjugate base The trichloromethyl anion then slowly decomposed to give dichlorocarbene [47]

$$B^\ominus + HCCl_3 \xrightarrow{\text{Fast}} {}^\ominus CCl_3 + BH$$

$$^\ominus CCl_3 \xrightarrow{\text{Slow}} :CCl_2 + Cl^\ominus$$
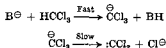
Further studies revealed that haloforms having two fluorine atoms tended to form difluorocarbene by a concerted loss of a proton and a halide ion.[48]

$$B^\ominus + HCXF_2 \rightarrow (B \cdots H \cdots CF_2 \cdots X)^\ominus \rightarrow :CF_2 + BH + X^\ominus$$
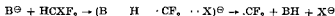
Hine and his co-workers have made extensive studies related to the hydrolysis of haloforms and the formation of halomethylenes from haloforms. The relative rates of formation of carbanions from haloforms is $CHI_3 \sim CHBr_2Cl > CHBrCl_2 > CHBrClF > CHBr_2F > CHCl_3 > CHBrClF > CHCl_2F$, showing that α-halogen substituents facilitate carbanion formation in the order $I \sim Br > Cl > F$.[45] The kinetics of hydrolysis of a number of haloforms in dioxane-water established the following order $CHBrClF > CHBrCl_2 > CHBr_2Cl \sim CHBr_2I > CHBr_3 > CHCl_3 \gg CHF_3$

The relative reactivities of the haloforms toward hydrolysis in aqueous solution have been correlated in terms of an equation based on the dihalomethylene reaction.[16][48] This equation uses the known carbanion formation rate constants and contains parameters for (1) the relative abilities of the various halogens to stabilize dihalomethylenes, (2) the relative ease with which halogens are separated as anions from the intermediate trihalomethyl anions, and (3) the carbanion character of the transition state for dihalomethylene formation. From the values of these parameters, halogens appear to facilitate dihalomethylene formation from $CX_3^\ominus$ in the order $F \gg Cl > Br > I$. This order is attributed to the relative abilities of the halogens to supply electrons to the carbon atom. The parameters for the differences between the abilities of halogen to separate as anions ($Br > I > Cl$) are smaller and probably less significant.

The formation of dichlorocyclopropanes from chloroform, an alkoxide, and an olefin is an excellent preparative procedure.[8] Potassium t-butoxide

[44] Hine and Langford, J. Am. Chem. Soc., 79, 5497 (1957).
[45] Hine, Burske, Hine, and Langford, J. Am. Chem. Soc., 79, 1406 (1957).
[46] Hine, Dowell, and Singley, J. Am. Chem. Soc., 78, 479 (1956)
[47] Hine and Dowell, J. Am. Chem. Soc., 76, 2688 (1954).
[48] Hine and Prosser, J. Am. Chem. Soc., 80, 4282 (1958).

is the base of choice.    Other alkoxides can be employed, but usually with
lower yields.    A competing reaction between dichlorocarbene and the
alcohol formed in the reaction lowers the yield of cyclopropane, and this
side reaction is slower with the more hindered alcohols.    Negatively
substituted olefins do not give cyclopropanes but react with the inter-
mediate trihalomethyl anion.[48a]

The reaction of bromoform with potassium $t$-butoxide and an olefin
leads to dibromocyclopropanes in good yield.[8,49,50] Fluoroform and
iodoform do not, however, lead to the formation of analogous products;
the iodoform is reduced to methylene iodide.[50]

The hydrolysis of mixed haloforms has been studied,[44,46,48,51-58] and
mixed haloforms have been used in the preparation of cyclopropanes as
illustrated by the accompanying equations.



(Ratio Br/Cl=3/1)                                                (Ref. 57)





(Ref. 58)



(Ref. 57)
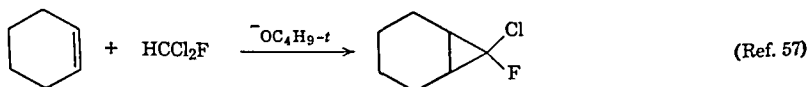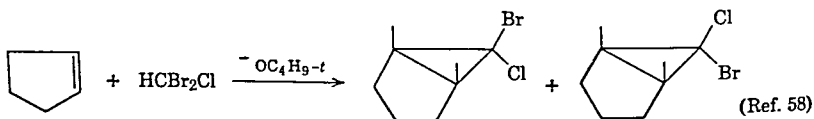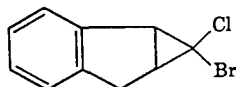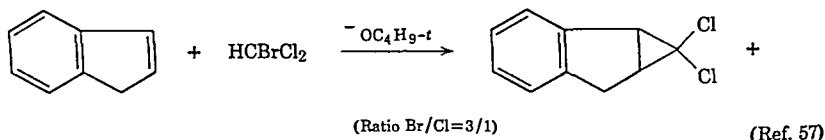
[48a] Bruson, Neiderhauser, Riener, and Hester, *J. Am. Chem. Soc.*, **67**, 601 (1945).
[49] Skell and Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).
[50] Parham, Reiff, and Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).
[51] Skell and Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).
[52] Hine and Porter, *J. Am. Chem. Soc.*, **82**, 6118 (1960).
[53] Hine, Ketley, and Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).
[54] Hine and Tanabe, *J. Am. Chem. Soc.*, **80**, 3002 (1958).
[55] Hine and Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957).
[56] Hine and Ketley, *J. Org. Chem.*, **25**, 606 (1960).
[57] Parham and Twelves, *J. Org. Chem.*, **22**, 7′       ---
[58] Skell and Sandler, *J. Am. Chem. Soc.*, **80**,

The reaction of olefins with dihalomethanes and an alkoxide leads to monohalocyclopropanes,[59-61] but the yields of adducts are poor The preferred method for generating monohalocarbenes is the reaction of dihalomethanes with an alkyllithium (see p 63)

**Alkoxide-Trihalocarbon Carbonyl Reaction.** The reaction of esters of trichloroacetic acid[13 62 63] or hexachloroacetone[11,64] with alkoxides in the presence of olefins leads to good yields of dichlorocyclopropanes No alcohol is formed in these reactions and the use of hindered alkoxides is not necessary.

$$RO^\ominus + Cl_3CCO_2R \rightleftharpoons Cl_3C\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle O^\ominus}{|}}{C}}OR \rightleftharpoons Cl_3C^\ominus + (RO)_2CO$$

$$Cl_3CCOCCl_3 + RO^\ominus \rightleftharpoons Cl_3C\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle O^\ominus}{|}}{C}}CCl_3 \rightleftharpoons Cl_3C^\ominus + Cl_3CCO_2R$$

$$Cl_3C^\ominus \rightarrow Cl^\ominus + CCl_2$$
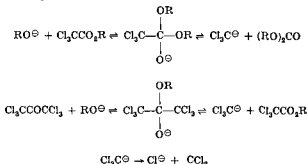
The dialkyl carbonate formed may be separated from the product by extraction with sulfuric acid or by distillation. Of the two equivalents of dichlorocarbene available from hexachloroacetone only one is utilized effectively, probably because some is lost through reaction with alkoxide ion (see p 59).

No comparable studies using trihaloacetates or haloacetones other than chloro compounds have been reported. Esters of dihaloacetic acids do not lead to monohalocarbenes. Instead derivatives of dihalocarbenes result, possibly as a consequence of an initial base-catalyzed disproportionation[62 63]

$$2Cl_2CHCO_2R \xrightarrow{\ominus OC_2H_5} Cl_3CCO_2R + ClCH_2CO_2R$$
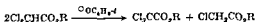
**Pyrolytic Reactions.** The thermal decomposition of salts of trihalo-acetic acids in 1,2-dimethoxyethane or bis-($\beta$ methoxyethyl) ether under

[59] Alexander, Herrick, and Roder, J Am Chem Soc, **72**, 2760 (1950)

[60] Volpin, Kursanov, and Dulova, Tetrahedron, **8**, 33 (1960)

[61] Dennstedt and Zimmermann, Ber, **18**, 3316 (1885)

[62] Parham, Loew, and Schweizer, J. Org Chem, **24**, 1900 (1959).

[63] Parham and Loew, J. Org Chem, **23**, 1705 (1958)

[64] Kadaba and Edwards, J. Org Chem, **25**, 1431 (1960).

reflux in the presence of an olefin leads to the formation of dihalocyclopropanes.[12,65,66] These reactions are thought to occur as follows.

$$X_3CCO_2M \rightarrow X_3C^{\ominus} + M^+ + CO_2$$
$$X_3C^{\ominus} + M^{\ominus} \rightarrow :CX_2 + MX$$
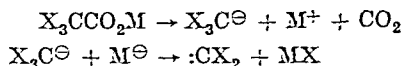
The yields of adducts are comparable to those obtained from haloforms. The method has been used for the generation of difluorocarbene[65] and is of special interest since it can be employed for the preparation of adducts of carbene acceptors that are sensitive to bases.

Silver trichloroacetate undergoes a side reaction forming carbon monoxide and trichloroacetyl chloride.[67-69]

Another useful pyrolytic reaction is that of phenyltribromomethyl- and phenyltrichloromethyl-mercury which, when heated in benzene, give the corresponding dihalonorcarane adduct with cyclohexene in 88% yield.[13a]

A number of other pyrolytic procedures that may proceed via a dihalocarbene have been reported.[70-77] These pyrolyses have been carried out in the absence of a carbene acceptor and result in products that could be derived from polymerization, dimerization, or disproportionation of several possible intermediates.

Thermal decomposition of trimethyltrifluoromethyltin appears to proceed via difluoromethylene since pyrolysis, alone or with tetrafluoroethylene, gives perfluorocyclopropane in high yield.[78]

$$3(CH_3)_3SnCF_3 \rightarrow 3(CH_3)_3SnF + \underset{CF_2}{\overset{CF_2-\!-\!-CF_2}{\diagdown\diagup}}$$
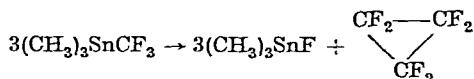
Thermal decomposition of certain halogeno-alkyl silicon compounds may also produce carbenes. Dichloronorcarane was obtained in 60% yield by allowing cyclohexene to react with trichloromethylsilicon trichloride at 250°.[79]

[65] Birchall, Cross, and Haszeldine, *Proc. Chem. Soc.*, 1960, 81.
[66] Wagner, Kloosterziel, and van der Ven, *Rec. Trav. Chim.*, 80, 740 (1961).
[67] Badea and Nenitzescu, *Angew Chem.*, 72, 415 (1960).
[68] Ioan, Badea, Cioranescu, and Nenitzescu, *Angew Chem.*, 72, 416 (1960).
[69] Beckurts and Otto, *Ber.*, 14, 576 (1881).
[70] Chambers, Clark, and Willis, *J. Am. Chem. Soc.*, 82, 5298 (1960).
[71] Semeluk and Bernstein, *J. Am. Chem. Soc.*, 79, 46 (1957).
[72] Haszeldine and Young, *Proc. Chem. Soc.*, 1959, 394.
[73] Atkinson and Atkinson, *J. Chem. Soc.*, 1957, 2086.
[74] Atkinson, *J. Chem. Soc.*, 1952, 2684.
[75] Park, Benning, Downing, Laucius, and McHarness, *Ind. Eng. Chem.*, 39, 354 (1947).
[76] Fink and Bonilla, *J. Phys. Chem.*, 37, 1135 (1933).
[77] Hodgins and Haines, *Can. J. Chem.*, 30, 473 (1952).
[78] Clark and Willis, *J. Am. Chem. Soc.*, 82, 1888 (1960).
[79] Bevan, Haszeldine, and Young, *Chem. & Ind. (London)*, 1961, 789.

$$Cl_3CSiCl_3 \xrightarrow{250°} SiCl_4 + :CCl_2 \xrightarrow{Cyclohexene}$$
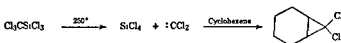


The reported isolation[80] of dichlorocarbene by pyrolysis of carbon tetrachloride has not been confirmed, however, difluoromethylene has been trapped at low temperature and identified as a product obtained by passage of radiofrequency discharge through certain fluorocarbons[81]

**Alkyllithium-Halocarbon Reactions.** The reaction of an alkyllithium with certain carbon tetrahalides in the presence of an olefin gives derivatives of dihalocyclopropanes[9] For example, dichloronorcarane has been prepared in 91% yield from bromotrichloromethane and cyclohexene.[9] The reaction proceeds by initial halogen-lithium exchange followed by loss of lithium halide to give the dihalocarbene. Difluorocarbene has also been prepared by this method from dibromodifluoromethane[82]

$$RLi + BrCCl_3 \rightarrow RBr + LiCCl_3$$
$$LiCCl_3 \rightarrow LiCl + CCl_2$$
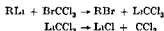
Dihalocarbenes can also be prepared from an alkyllithium and a haloform[83]

$$RLi + HCX_3 \rightarrow RH + LiCX_3 \rightarrow LiX + CX_2$$

However, when this reaction was carried out in the presence of olefins relatively low yields of adducts resulted, and the reaction appears to be of little synthetic value

The most important application of the alkyllithium-halocarbon reaction is its use for the synthesis of monochlorocarbene.[10][83] Closs and his co-workers have shown that this procedure is the best method for the synthesis of many monochlorocyclopropanes

$$RCH_2Li + CH_2Cl_2 \longrightarrow RCH_3 + LiCHCl_2$$

$$LiCHCl_2 \longrightarrow LiCl + :CHCl$$
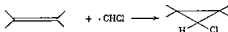
[80] Schmeisser and Schröter, *Angew Chem*, 72, 349 (1960)
[81] Mastrangelo, *Abstr*, 140th *Am Chem Soc*, September, 1961, p. 6M.
[82] Franzen, *Angew Chem*, 72, 566 (1960)
[83] Closs and Closs, *J Am Chem Soc*, 82, 5723 (1960)

The predominant side reaction observed is the formation of the olefin $RCH{=}CH_2$ from the alkyllithium $RCH_2Li$. The olefin is thought to result from the reaction of monochlorocarbene with $RCH_2Li$ followed by loss of lithium chloride and a 1,2-hydride shift.

$$RCH_2Li + {:}CHCl \rightarrow RCH_2\overset{\displaystyle H}{\underset{\displaystyle Cl}{-\overset{|}{\underset{|}{C}}-}}Li$$

$$RCH_2\overset{\displaystyle H}{\underset{\displaystyle Cl}{-\overset{|}{\underset{|}{C}}-}}Li \rightarrow LiCl + RCH_2CH{:}$$
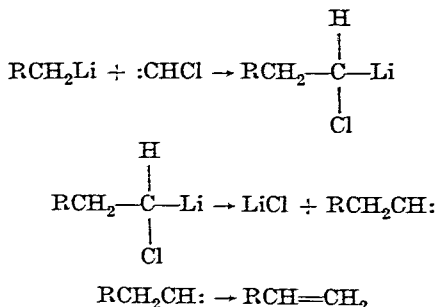
$$RCH_2CH{:} \rightarrow RCH{=}CH_2$$

Along with the olefin $RCH{=}CH_2$, some cyclopropane corresponding to an intramolecular insertion reaction of $RCH_2CH{:}$ is also formed.[83a]  When

$$RCH_2CH_2CH{:} \rightarrow RCH_2CH{=}CH_2 + RCH\underset{\displaystyle CH_2}{-}CH_2$$
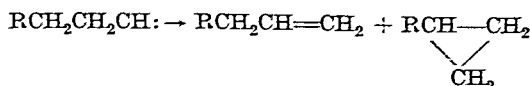
methylene chloride is added to excess alkyllithium, the reaction of the alkyllithium with chlorocarbene predominates and terminal olefins are formed in high yield.[10,83]

### REACTIONS OF HALOCARBENES

**With Alkenes, Cycloalkenes, and Alkynes.**  The principal reaction of halocarbenes with olefins is addition to form halocyclopropanes, and the order of reactivity of carbenes appears to be $CH_2 > CHCl > CCl_2 > CBr_2 > CF_2$.[14,60,83-87]  This order is consistent with added stabilization provided by overlap of the unshared $p$-electrons of the halogen with the vacant $p$-orbital of the carbene.

The halocarbenes are electrophilic in character, and the relative rates of their additions to carbon-carbon double bonds generally increase with increasing alkyl substitution at the olefin function.[14,49,83,85]  Steric factors appear to be less important in this respect than electronic factors.[14,50,87,89]

[83a] Closs, *Abstr. 135th Meeting, Am. Chem. Soc.*, Sept., 1960, p. 9P.
[84] Doering and Henderson. *J. Am. Chem. Soc.*, 80, 5274 (1960).
[85] Doering, Buttery. Laughlin, and Chaudhuri, *J. Am. Chem. Soc.*, 78, 3224 (1956).
[86] Ledwith and Bell, *Chem. & Ind. (London)*, 1959, 459.
[87] Closs and Schwartz, *J. Am. Chem. Soc.*, 82, 5729 (1960).
[88] Woodworth and Skell, *J. Am. Chem. Soc.*, 79, 2542 (1957).
[89] Parham and Wright, *J. Org. Chem.*, 22, 1473 (1957).
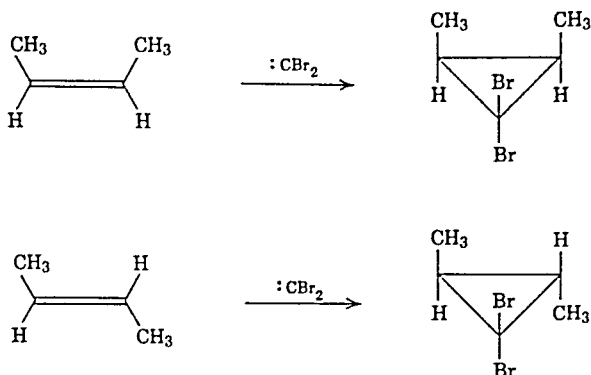
The reaction of monochlorocarbene with cyclohexene gives two isomers that were tentatively assigned the *endo* **1** and *exo* **2** structures.[83]
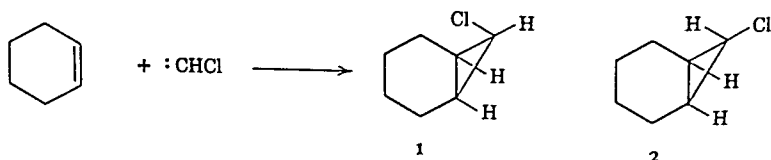


Differences in *cis/trans* ratios are also noted with olefins that react more slowly than cyclohexene, and it seems probable that steric factors alone can provide only a partial explanation of these observations. For example, *cis/trans* ratios for the products from monochlorocarbene and *cis*-2-butene and 2-methyl-2-butene are 1:5.5 and 1:1.6, respectively.[83]
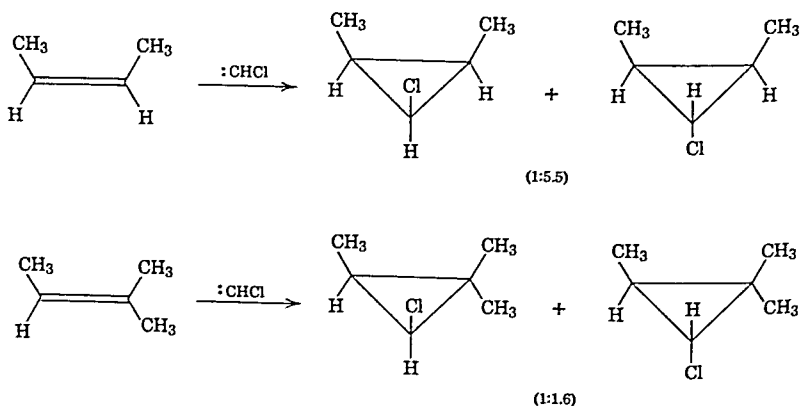
Dichloro- and dibromo-carbene add to 1,3-dienes to give vinylcyclo-propanes,[56,88,85,91,92] there is no evidence for 1,4-addition Thus dichloro-carbene reacts with butadiene to give 3 and 4 but not 5.[91]

$$CH_2=CH—CH=CH_2 + .CCl_2 →$$
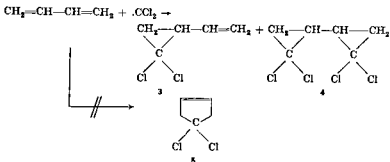


Dibromocarbene[93] adds similarly to 1,2-dienes to give methylenecyclo-propane derivatives (40–60% yield) Such additions are reported to occur exclusively at the more highly alkylated double bond.
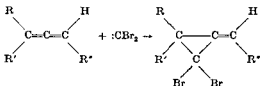


Hydrocarbons containing both double and triple bonds have been treated with dihalocarbenes. The only products reported from the reac-tions of dichloro- and dibromo-carbene with conjugated ene-ynes were those derived from additions to the carbon-carbon double bonds.[84,95]

Dihalocarbenes add to internal triple bonds to form dihalocyclo-propenes,[95–98] which have been useful intermediates for the preparation of cyclopropenones Attempts to prepare halocyclopropenes from terminal acetylenes have been unsuccessful.[95,98]

[85] Orchin and Herrick, J. Org Chem, 24, 139 (1959).

[86] Skeno and Oda, J. Chem Soc. Japan, Pure Chem Sect, 80, 1200 (1959).

[87] Ball and Lander, Proc Chem Soc, 1961, 246

[88] D'yackonova, Favorskaya, Danilkina, and Auvinen, J. Gen. Chem. USSR (English Transl) 30, 3475 (1960) [C.A., 65, 19814 (1961)]

[92] Vo-Quang and Cadiot, Compt Rend, 252, 3827 (1961).

[93] Breslow and Peterson, J. Am Chem. Soc, 82, 4426 (1960).

[97] Volpin, Koreshkov, and Kursanov, Izv Akad Nauk SSSR, 1959, 560 [C.A., 53, 21789 (1959)]

[98] Kursanov, Volpin, and Koreshkov, J Gen Chem USSR, (English Transl), 30, 2855 (1960) [C.A, 55, 16473 (1961)]

**With Aromatic Carbon-Carbon Double Bonds.** Dichlorocarbene reacts only with difficulty with aromatic double bonds, and many reactions involving dihalocarbene have been effected by using benzene as solvent.[60,86,89,99,100] Reaction generally occurs with electron-rich aromatic compounds.

The formation of a small amount of a chloroazulene from indene and dichlorocarbene results from attack of the carbene on an aromatic double bond.[101]
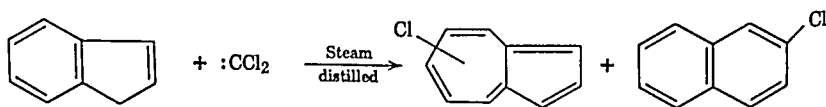


Chlorotropones are produced when dichlorocarbene reacts with alkoxynaphthalenes.[100]
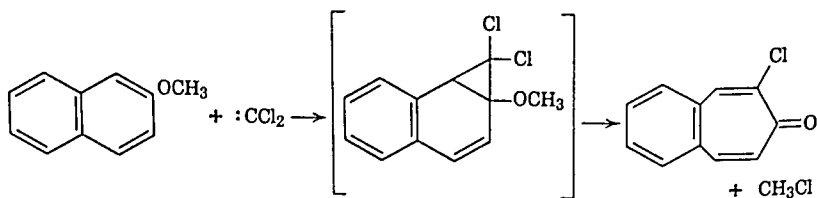


With 9-methoxyphenanthrene, the intermediate dichlorocyclopropane was isolated in 52% yield and converted by heat to the dibenzchlorotropone in high yield.
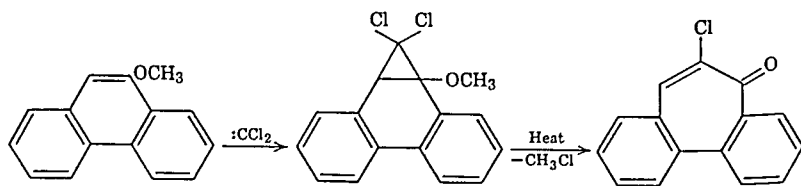


No report has yet been made of the interaction of dihalocarbenes with naphthalene or phenanthrene, but anthracene reacts with dichlorocarbene to form a chlorotropilium salt that is converted to 6 by the action of base.[102] Treatment of 6 with acid regenerates the tropilium salt.

[99] Closs and Closs, *Tetrahedron Letters*, **10**, 38 (1960).
[100] Parham, Bolon, and Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961).
[101] Parham and Reiff, *J. Am. Chem. Soc.*, **77**, 1177 (1955).
[102] Murray, *Tetrahedron Letters*, **7**, 27 (1960).
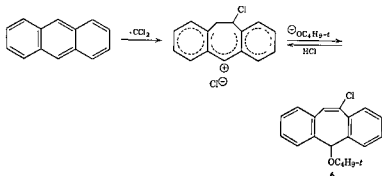
Monochlorocarbene, which is more reactive than dichlorocarbene, reacts readily with benzene to give derivatives of cycloheptatriene[60,99] The
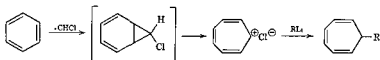


reaction of methyllithium with lithium phenoxide in methylene chloride occurs in a similar manner and yields 2 methyl 3,5-cycloheptadienone.[103] A variety of substituted phenoxides reacts to form similar products

Many ring expansions of pyrroles[33,37,59,61,104-106] and indoles[33,106] to form pyridines and quinolines have been reported An example is the conversion of indole to quinoline by the action of methyllithium and methylene chloride[106]
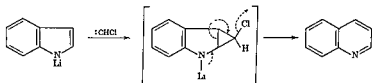


**With Carbon-Nitrogen Double Bonds.** The only reaction of this type that has been reported is that of dichlorocarbene with benzanaline to form 7[64,107] The product is rapidly hydrolyzed to N-phenyl-α-chloro-phenylacetamide

[103] Closs and Closs, J Am Chem Soc, **83**, 599 (1961)
[104] Ciamician and Dennstedt, Ber, **15**, 1172 (1882)
[105] Ciamician and Silber, Ber, **20**, 191 (1887)
[106] Closs and Schwartz, J Org Chem, **26**, 2609 (1961)
[107] Fields and Sandri, Chem & Ind (London), 1959, 1216

$$C_6H_5CH=NC_6H_5 \xrightarrow{\ :CCl_2\ } C_6H_5CH\underset{\displaystyle \underset{7}{\overset{\displaystyle C}{\diagup \diagdown}}}{\text{———}}NC_6H_5$$

$$Cl \qquad Cl$$
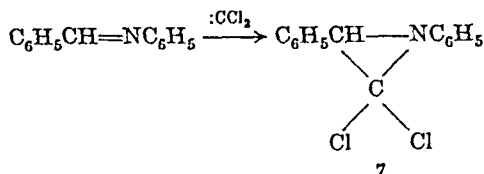
**Miscellaneous Reactions.** Detailed review of the many other reactions of halocarbenes is beyond the scope of this chapter. Some of the most important ones are summarized here primarily to provide a convenient key to the literature on this aspect of halocarbene chemistry.

Early work showed that carbon monoxide and orthoformates were formed from dihalocarbenes and alcohols.[29–31,108] Modern techniques have led to the identification of many other products from these reactants.[51,53–55,109,110]

Secondary and tertiary amines react with dichlorocarbene to give amides after hydrolysis of the intermediates.[7,111] Primary amines react with

$$C_6H_5CH_2N(CH_3)_2 \xrightarrow{\ :CCl_2\ } \left[ \begin{array}{c} C_6H_5CH_2\overset{\oplus}{N}(CH_3)_2 \\ | \\ CCl_2 \\ \ominus \end{array} \right] \longrightarrow$$

$$C_6H_5CH_2CCl_2N(CH_3)_2 \xrightarrow{\ H_2O\ } C_6H_5CH_2CON(CH_3)_2$$
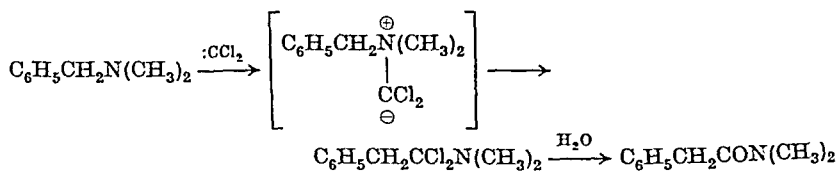
dichlorocarbene in non-aqueous media to form isocyanides.[6,112] This observation supports the proposed mechanism of the Hofmann isocyanide synthesis.[6,7]

Triphenylphosphine reacts with dichlorocarbene to give dichlorophosphine methylene, which has been used in the Wittig reaction to prepare terminal dichloroölefins, $RCH=CCl_2$.[113,114] Wittig reagents have been similarly prepared from monochlorocarbene[115,116] and difluorocarbene.[82]

Difluorocarbene has been allowed to react with a number of anions to give difluoromethyl derivatives.[117] For instance diethyl phenyldifluoromethylmalonate was obtained in 80% yield by allowing difluorocarbene to react with the sodium salt of diethyl phenylmalonate.[117]

[108] Nef, *Ann.*, **308**, 329 (1899).

[109] Hine and Tanabe, *J. Am. Chem. Soc.*, **79**, 2654 (1957).

[110] Hine, Pollitzer, and Wagner, *J. Am. Chem. Soc.*, **75**, 5607 (1953).

[111] Saunders and Murray, *Tetrahedron*, **6**, 88 (1959).

[112] Krapcho, *J. Org. Chem.*, **27**, 1089 (1962).

[113] Speziale, Marco, and Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960).

[114] Speziale, Ratts, and Marco, *Abstr., 140th Meeting, Am. Chem. Soc.*, September 1961, p. 35Q.

[115] Seyferth, Grim, and Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960).

[116] Seyferth, Grim, and Read, *J. Am. Chem. Soc.*, **83**, 1617 (1961).

[117] Shen, Lucas, and Sarett, *Tetrahedron Letters*, **2**, 43 (1961).

## REACTIONS OF HALOCYCLOPROPANES

The halocyclopropanes undergo transformations leading either to ring expansion, chain lengthening, or formation of a second cyclopropane ring and are thus valuable synthesis intermediates

The first example of ring expansion was the quantitative conversion of the cyclopropane derivative 8 to 2 chloronaphthalene [50]
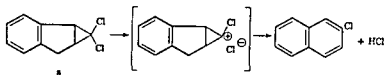


Similar reactions starting with a variety of substituted indenes have been carried on [50 57 61 101] Preliminary studies have shown that the rates of these reactions are unaffected by added alkali[50] but are increased by added silver ion [55]

The bicyclo [3 1 0] system of 9 is 200 times as reactive as the analogous [4 1 0] system in dibromonorcarane [56] The reason for this greatly enhanced rate is thought to be the relief of the greater strain in the [3.1 0] system
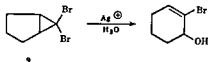


An interesting steric requirement for these ring expansion reactions was noted for mixed halides obtained from indene [57] The ratio of 2-chloro- and 2-bromo-naphthalene obtained was approximately 1·1.
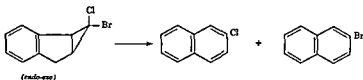


(endo-exo)

The α- and β-isomers (endo-exo) of 2-bromo-2 chlorobicyclo[3 1 0]hexane (10, X = Cl, Y = Br) have been isolated,[59] but their absolute configurations have not been determined.

**10**
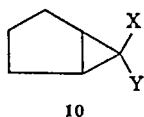
Dihalocyclopropanes are decomposed thermally, and the ease of ring expansion is a function of structure.   Dichloronorcarane gives cyclohepta-



triene and toluene by pyrolysis at 490°.[118]    The analogous 2-oxa-7,7-di-chlorobicyclo[4.1.0]heptane gives 3-chloro-6,7-dihydroöxepine at 140°.[119]
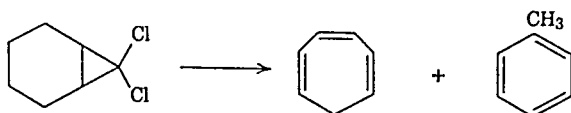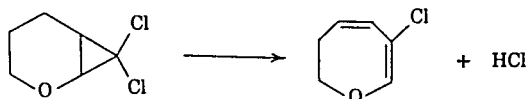


The two isomers of 2-oxa-7-chloronorcarane differ strikingly in their reactivity.   One, tentatively identified as *exo*, gives the dihydroöxepine by reaction at 140° in quinoline.   Under these conditions the other, supposedly *endo*, isomer is unaffected.
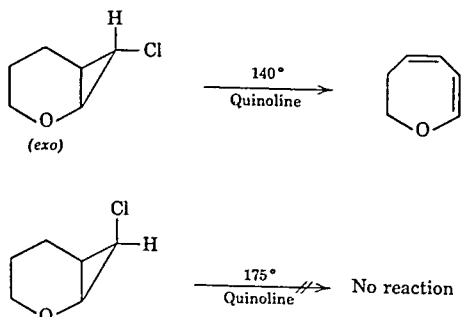


It is probable that relief of strain, relative stability of possible intermediate ions, and anchimeric assistance by hetero atoms all may be involved in determining the ease with which a particular halocyclopropane undergoes this type of reaction.

Similar reactions applied to halocyclopropanes bearing aliphatic rather than cycloaliphatic substituents produce a chain-lengthening process by

[118] Winberg, *J. Org. Chem.*, **24**, 264 (1959).
[119] Schweizer and Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

insertion of a new atom *between* the doubly bonded atoms of the original olefin [58]

$$R_2C=CR_2 \xrightarrow{CCl_4} R_2C\underset{\underset{Cl}{\overset{C}{|}}{\overset{CCl_2}{}} CR_2 \xrightarrow{Ag^{\oplus}}{H_2O} R_2C=C\underset{\underset{Cl}{|}}{\overset{CR_2}{}} CR_2$$
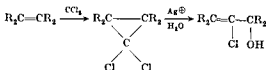
A generally applicable method of chain lengthening is the conversion of halocyclopropanes to allenes This reaction, discovered by Doering, involves reaction of the dibromocyclopropane with sodium or magnesium [129] The yields of allenes are quite high, however, some isomeric

$$R_2C\underset{\underset{Br}{\overset{C}{|}}{\overset{CBr_2}{}} CR_2 \xrightarrow{Na \text{ or } Mg} R_2C=C=CR_2$$
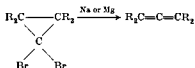
products are also formed [120–122] The reaction has been extended under different conditions to dichlorocyclopropanes [123,124] High yields of purer allenes are obtained when dibromocyclopropanes are allowed to react with an alkyllithium,[123,125] and this method is convenient for the synthesis of cyclic and acyclic allenes. These reactions with alkyllithiums have been shown to involve carbene intermediates by studies with dibromonorcarane.
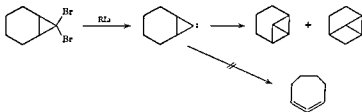


Collapse of the intermediate bicyclic carbene to the cyclic seven-membered ring allene is sterically unfavorable; intramolecular insertion to give highly strained bicyclic systems results.[126,127]

[120] Doering and LaFlamme, *Tetrahedron*, **2**, 75 (1958)
[121] Gardner and Narayana, *J Org Chem*, **26**, 3518 (1961)
[122] Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961)
[123] Ball and Landor, *Proc. Chem Soc*, 1961, 143
[124] Logan, *Tetrahedron Letters*, **5**, 173 (1961)
[125] Moore and Ward, *J Org Chem*, **25**, 2073 (1960).
[126] Moore, Ward, and Merritt, *J Am Chem Soc*, **83**, 2019 (1961).
[127] Moore and Ward, *Chem & Ind (London)*, 1961, 594

The 2,2-dihalocyclopropanone acetals, prepared by addition of dihalo-carbene to ketene acetals, may be converted to α-chloroacrylic esters by heat or to orthopropiolates by base.[128]

$$
\begin{array}{c}
\text{H}_2\text{C}\!\!-\!\!\text{C(OC}_2\text{H}_5)_2 \\
\diagdown\ \text{C}\ \diagup \\
\text{Cl}\quad\text{Cl}
\end{array}
\xrightarrow{\ \text{Heat}\ }
\left[
\begin{array}{c}
\text{Cl} \\
| \\
\text{CH}_2\!\!=\!\!\text{C}\!\!-\!\!\overset{\oplus}{\text{C}}(\text{OC}_2\text{H}_5)_2 \\
\text{Cl}^{\ominus}
\end{array}
\right]
\rightarrow
\begin{array}{c}
\text{Cl} \\
| \\
\text{CH}_2\!\!=\!\!\text{C}\!\!-\!\!\text{CO}_2\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{Cl}
\end{array}
$$

$$
\xrightarrow{\ \ominus\text{OC}_4\text{H}_9\text{-}t\ }
\left[
\begin{array}{c}
\text{H}_2\text{C}\!\!-\!\!\text{C(OC}_2\text{H}_5)_2 \\
\diagdown\ \text{C}\ \diagup \\
| \\
\text{Cl}
\end{array}
\right]
\rightarrow
\begin{array}{c}
\text{OC}_4\text{H}_9\text{-}t \\
| \\
\text{HC}\!\equiv\!\text{C}\!\!-\!\!\text{C(OC}_2\text{H}_5)_2
\end{array}
$$
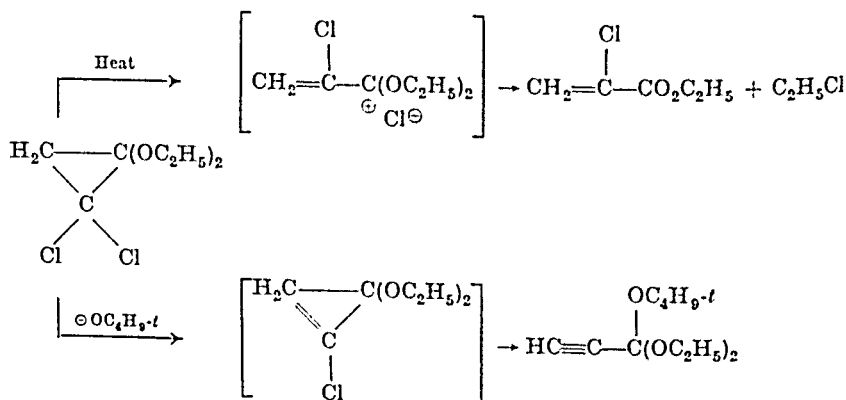
The propiolate reaction is thought to proceed through the cyclopropene. Additional evidence in support of this view is the reaction of phenyl-chlorocarbene with phenylketene acetal and transformation of the inter-mediate to 2,3-diphenylcyclopropenone.[129]

$$
\text{C}_6\text{H}_5\text{CH}\!\!=\!\!\text{C(OCH}_3)_2
\xrightarrow[\text{KOC}_4\text{H}_9\text{-}t]{\text{C}_6\text{H}_5\text{CHCl}_2}
\left[
\begin{array}{c}
\text{C}_6\text{H}_5\text{CH}\!\!-\!\!\text{C(OCH}_3)_2 \\
\diagdown\ \text{C}\ \diagup \\
\text{C}_6\text{H}_5\quad\text{Cl}
\end{array}
\right]
\rightarrow
$$

$$
\left[
\begin{array}{c}
\text{C}_6\text{H}_5\text{C}\!\!-\!\!\text{C(OCH}_3)_2 \\
\diagdown\ \text{C}\ \diagup \\
| \\
\text{C}_6\text{H}_5
\end{array}
\right]
\rightarrow
\begin{array}{c}
\text{C}_6\text{H}_5\text{C}\!\!=\!\!\text{CC}_6\text{H}_5 \\
\diagdown\ \text{C}\ \diagup \\
|| \\
\text{O}
\end{array}
$$
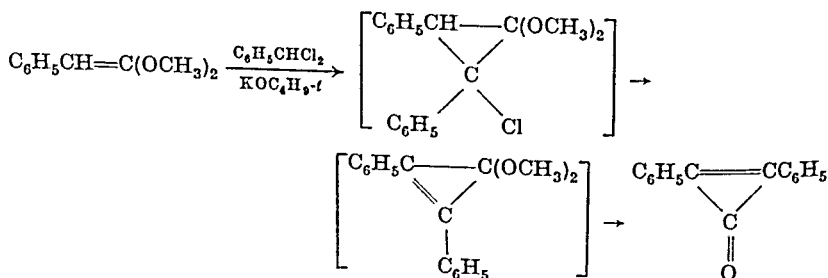
## EXPERIMENTAL PROCEDURES

**7,7-Dichlorobicyclo[4.1.0]heptane.** *A.* (Using chloroform as the carbene source.[8]) A stirred mixture of 1.5 l. of dry *t*-butyl alcohol (distilled from aluminum *t*-butoxide) and 60 g. (1.5 moles) of potassium metal is allowed to react at the boiling point of the alcohol. The alcohol is then removed by distillation and the residue is dried at 150–160°/1–2 mm. for 2 hours. The dried solid is powdered manually and covered with 1.5 l. of cyclohexene. To the resulting mixture, cooled in an ice bath,

[128] McElvain and Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

[129] Breslow, Haynie, and Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

reagent grade methylene chloride (17 g., 0.2 mole) under an atmosphere of nitrogen. The mixture is hydrolyzed, the organic layer separated, washed, and dried over magnesium sulfate. Distillation gives 8.8 g. (67%) of 1-chloro-2,2,3,3-tetramethylcyclopropane, b.p. 72°/105 mm., $n_D^{20}$ 1.4458.

**2-Oxa-7-chlorobicyclo[4.1.0]heptane.**[119] Commercial *n*-butyllithium (3.54 moles) in heptane is added dropwise during 4 hours to a cold (−10° to −20°) mixture of dry dihydropyran (378 g., 4.5 moles) and dry methylene chloride (382 g., 4.5 moles). The mixture is allowed to warm to room temperature and is stirred overnight. Water (600 ml.) is added, the mixture is filtered, and the organic layer separated. The aqueous layer is extracted three times with 400-ml. portions of petroleum ether (b.p. 30–60°), and the combined organic layers are dried over anhydrous magnesium sulfate. Distillation furnishes 134 g. (28%) of a mixture of the racemic isomers of 2-oxa-7-chlorobicyclo[4.1.0]heptane, b.p. 45–48°/3–1.5 mm., $n_D^{25}$ 1.4798–1.4879. The mixture is separated by fractionation into *endo*-2-oxa-7-chloronorcarane (b.p. 34.0°/1.1 mm., $n_D^{25}$ 1.4765) and *exo*-2-oxa-7-chloronorcarane (b.p. 48°/1.5 mm., $n_D^{25}$ 1.4873).

**2,7-Di-*t*-butyltropone.**[103] Methyllithium (0.41 mole) in diethyl ether (230 ml.) is added over a period of 2.5 hours to a solution of 2,6-di-*t*-butylphenol (48 g., 0.23 mole) in 250 ml. of methylene chloride at room temperature. After hydrolyzing in ice water, the organic layer is washed consecutively with dilute hydrochloric acid, aqueous sodium bicarbonate, and water. Removal of the solvent and distillation give 34.5 g. (0.17 mole) of 2,6-di-*t*-butylphenol (b.p. 57–58°/0.15 mm.) and crude 2,7-di-*t*-butyltropone (b.p. 76–82°/0.15 mm.). Redistillation of the crude product yields 9.1 g. of 2,7-di-*t*-butyltropone boiling at 67–70°/0.10 mm. (70% based on recovered 2,6-di-*t*-butylphenol). Recrystallization of the tropone twice from pentane gives an analytical sample, m.p. 70.5°.

## TABULAR SURVEY

Tables I through IV encompass the reactions of dihalocarbenes. Monohalocarbenes are surveyed in Table V. The tables are arranged according to the nature of the halide, in the following order: chlorine, bromine, iodine, fluorine. The acceptors in each table under a given halocarbene are arranged in order of increasing number of carbon atoms.

Where more than one reference is cited, the experimental data are taken from the experiment reporting the highest yield; this reference is cited first. Where the yield is not given, a dash is placed in the yield column.

The literature through November 1, 1961, and a few more recent references are included in the text and tables.

TABLE I

Reactions of Dichlorocarbene with Alkenes, Alkynes, and Cycloalkenes

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs |
|---|---|---|---|---|---|
| 2 Methyl-1-propene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2,2-dimethylcyclopropane | 65 | 8, 63, 84 |
| | CCl₃CO₂C₂H₅ | NaOCH₃ | 1,1-Dichloro-2,2-dimethylcyclopropane | 76 | 13 |
| | CCl₃CO₂C₄H₉-t | KOC₄H₉-t | 1,1-Dichloro-2,2-dimethylcyclopropane | 86 | 13, 63 |
| | CCl₃CO₂K | * | Di-t-butyl carbonate | 89 | |
| | | | 1,1-Dichloro-2,2-dimethylcyclopropane | 60 | 66 |
| | CHCl₂CO₂C₂H₅ + (CH₃)₃COCl | KOC₄H₉-t | 1,1-Dichloro-2,2-dimethylcyclopropane | 13 | 63 |
| | | | Di-t-butyl carbonate | 16–20 | |
| | | | Hexa-t-butyl melitate | 3 | |
| | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2,2-dimethylcyclopropane | 55 | 62 |
| | | | t-Butyl trichloroacetate | 5 | |
| 1,3-Butadiene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro 2 vinylcyclopropane | 51 | 88, 91 |
| | | | 1,1-Dichloro-2,2-dimethylcyclopropane | Trace | |
| | CCl₃CO₂Na | | 2,2'-Bis[1,1-dichlorocyclopropyl]cyclopropane | Trace | |
| 1 Pentene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-propylcyclopropane | 70 | 66 |
| cis-2-Pentene | CHCl₃ | KOC₄H₉-t | cis 1,1-Dichloro-2-methyl-3-ethylcyclopropane | — | 84 |

Note
* The reactants were heated at reflux.

TABLE I—*Continued*

REACTIONS OF DICHLOROCARBENE WITH ALKENES, ALKYNES, AND CYCLOALKENES

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| 2-Methyl-1-butene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-methyl-2-ethylcyclopropane | — | 84 |
| 2-Methyl-2-butene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2,2,3-trimethylcyclopropane | 66 | 8, 84 |
|  | (CCl₃)₂CO | NaOCH₃ | 1,1-Dichloro-2,2,3-trimethylcyclopropane | 23 | 64 |
|  |  |  | 1,1,1,3,3,3-Hexachloro-2-propanol | — | — |
| 2-Methyl-1,3-butadiene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-methyl-2-vinylcyclopropane | 37 | 91, 86; 92 |
| 2-Methyl-1-buten-3-yne | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-methyl-2-ethynylcyclopropane | 65 | 95 |
| Cyclopentadiene | CHCl₃ | Na | Chlorobenzene | 23 | 130 |
| 1-Hexene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-n-butylcyclopropane | — | 84 |
|  | CHCl₃ | KOC(CH₃)₂C₂H₅ | 1,1-Dichloro-2-n-butylcyclopropane | 16 | 8 |
| 1,5-Hexadiene | CCl₃CO₂Na | * | 1,1-Dichloro-2-[butenyl-3]cyclopropane | 23 | 66 |
| 2,3-Dimethyl-2-butene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2,2,3,3-tetramethylcyclopropane | — | 84 |
|  | CCl₃CO₂Na | * | 1,1-Dichloro-2,2,3,3-tetramethylcyclopropane | 87 | 66 |
|  | CCl₄ | † | 1,1-Dichloro-2,2,3,3-tetramethylcyclopropane | — | 131 |

| Reactants | Reagent | Reagent | Product | Major product (%) | References |
|---|---|---|---|---|---|
| 2,3-Dimethyl-1,3-butadiene | CHCl₃ | KOC₄H₉ | 2,4-Dichloro-1-methyl-1-isopropenylcyclopropane | 20 | 92 |
| 2-Methyl-1-penten-3-yne | CCl₃CO₂Na | | 1,1-Dichloro-2-methyl-2-[1-propynyl]cyclopropane | 94 | 94 |
| Cyclohexene | CHCl₃ | n-C₄H₉Li | 7,7-Dichlorobicyclo[4.1.0]heptane | 91 | 9 |
| | CCl₃CO₂CH₃ | NaOCH₃ | 7,7-Dichlorobicyclo[4.1.0]heptane | 70–88 | 13 |
| | CHCl₃ | * | 7,7-Dichlorobicyclo[4.1.0]heptane | 88 | 13a |
| | CCl₄ | * | 7,7-Dichlorobicyclo[4.1.0]heptane | 71 | 9 |
| | (CCl₃)₂CO | KOC₄H₉ | 7,7-Dichlorobicyclo[4.1.0]heptane | 67 | 9 |
| | CCl₄ | NaOCH₃ | 7,7-Dichlorobicyclo[4.1.0]heptane | 65 | 12,66 |
| | CHCl₃ | n-C₄H₉Li | 7,7-Dichlorobicyclo[4.1.0]heptane | 60 | 79 |
| | CHBr₃ | KClHC(CH₃)₂ | 7,7-Dibromobicyclo[4.1.0]heptane | 59 | 8,84 |
| | CHBr₃ | n-C₄H₉Li | 7,7-Dibromobicyclo[4.1.0]heptane | 59 | 11,64 |
| | CHBr₃ | KClHC(CH₃)₂ | 7,7-Dibromobicyclo[4.1.0]heptane | 50 | 9 |
| | CCl₄ | n-C₄H₉Li | 7,7-Dibromobicyclo[4.1.0]heptane | 38 | 118 |
| | CHBr₃ | NaOCH₃ | 7,7-Dibromobicyclo[4.1.0]heptane | 28 | 132 |
| | CHCl₃ | * | 7,7-Dichlorobicyclo[4.1.0]heptane | 19 | 83 |
| | CHBr₃ | | 7,7-Dibromobicyclo[4.1.0]heptane | 17 | 132 |
| | CHBr₃ | | 7,7-Dibromobicyclo[4.1.0]heptane | 15 | 132 |
| | CCl₄ | | 7,7-Dichlorobicyclo[4.1.0]heptane | 8 | 9 |
| | CHBr₃ | | 7,7-Dibromobicyclo[4.1.0]heptane | 10 | 15 |
| | CCl₃CO₂Ag | | 7,7-Dichlorobicyclo[4.1.0]heptane | | 8 |
| | | | 7,7-Dibromobicyclo[4.1.0]heptane | | 10 |
| Cyclohexene oxide | CCl₃CO₂Ag | | Trichloroacetic anhydride | — | 68,69 |
| 2-Methyl 2-hexen-4-yne | CCl₃CO₂Na | * | Unchoaracterized | 20 | 94 |

\* The reactants were heated at reflux.

† Electrolysis in acetonitrile at −20°

‡ The reactants were heated under reflux in benzene.

§ The reactants were heated at 250°.

TABLE I—*Continued*

REACTIONS OF DICHLOROCARBENE WITH ALKENES, ALKYNES, AND CYCLOALKENES

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| 3-Ethyl-2-penten-4-yne | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-ethyl-2-ethynyl-3-methylcyclopropane | 40 | 95 |
| 1-Ethynylcyclopentene | CHCl₃ | KOC₄H₉-t | 1-Ethynyl-6,6-dichlorobicyclo[3.1.0]hexane | — | 133 |
| 1-Methylcyclohexene | — | — | 1-Methyl-7,7-dichlorobicyclo[4.1.0]heptane | 20 | 130 |
| Cycloheptatriene | CHCl₃ | NaOCH₃ | 8,8-Dichlorobicyclo[5.1.0]octa-3,5-diene | 46 | 12, 66 |
| | CCl₃CO₂Na | * | 8,8-Dichlorobicyclo[5.1.0]octa-3,5-diene | — | 124 |
| 1-Octene | — | — | 1,1-Dichloro-2-hexylcyclopropane | — | 8 |
| 4-Vinylcyclohexene | CHCl₃ | KOC₄H₉-t | Unidentified | 50 | 8 |
| β-Pinene | CHCl₃ | KOC₄H₉-t + t-C₄H₉OH | Unidentified | — | 86 |
| Ethylbenzene | CHCl₃ | KOC₄H₉-t | None | 76 | 134 |
| Styrene | CHCl₃ | KOC₄H₉-t | 1,1-Dichloro-2-phenylcyclopropane | — | 86 |
| Phenylacetylene | CHCl₃ | KOC₄H₉-t | None | 45 | 95 |
| 1-Ethynylcyclohexene | CHCl₃ | KOC₄H₉-t | 1-Ethynyl-6,6-dichlorobicyclo[4.1.0]heptane | — | 135 |
| Cycloöctatetraene | CHCl₃ | KOC₄H₉-t | 9,9-Dichlorobicyclo[6.1.0]nona-2,4,6-triene | | |

| Reactant | CCl₃CO₂C₂H₅ CCl₃CO₂Na | NaOCH₃ | CHCl₃ | KOC₄H₉t | Product | | References |
|---|---|---|---|---|---|---|---|
| Di-n-propylacetylene | — | — | — | — | Di-n propylcyclopropene | 5‖ | 96 |
| 1-Dodecene | — | * | — | — | 1,1 Dichloro 2-decylcyclopropane | — | 96 |
| 1-Cyclohexylcyclohexene | — | — | — | — | 1-Cyclohexyl-7,7 dichlorobicyclo[4 1 0]heptane | — | 124 |
| 1-Phenylcyclohexene | — | — | — | — | 1-Phenyl-7,7 dichlorobicyclo[4 1 0]heptane | — | 133 |
| Diphenylacetylene | — | — | CHCl₃ | — | Diphenylcyclopropenone | 24‖ | 98, 97 |
| 1-α-Naphthylcyclohexene | — | — | — | KOC₄H₉t | 1-α-Naphthyl 7,7 dichlorobicyclo[4 1 0]heptane | — | 133 |
| 1 Octadecene | — | — | — | — | 1,1 Dichloro-2-hexadecylcyclopropane | — | 124 |

Note. References 130 to 140 are on p. 90.
* The reactants were heated at reflux.
‖ The product was obtained as the hydrochloride after hydrolysis of the adduct.

| Reactant | Reagent | Product | Yield (%) | References |
|---|---|---|---|---|
| Cyclohexene | $C_6H_5HgCBr_3$ | 7,7-Dibromobicyclo[4.1.0]heptane | 88 | 13a |
|  | $CHBr_3$ * | 7,7-Dibromobicyclo[4.1.0]heptane | 75 | 8, 14 |
|  | $KOC_4H_9$-t | 7,7-Dibromobicyclo[4.1.0]heptane | 11 | 84 |
| 1,4-Cyclohexadiene | $CBr_4$ / $CHBr_3$ | 7,7-Dibromobicyclo[4.1.0]heptane | 70 | 9 |
|  | $LiC_4H_9$-n / $CHBr_3$ | 7,7-Dibromobicyclo[4.1.0]-3-heptene | 1 | 136, 137, 138 |
|  |  | [structure, $Br_2$] |  | 123 |
| Cycloheptene | $CHBr_3$ | 8,8-Dibromobicyclo[5.1.0]octane | 33 | 121, 122, 123 |
| Cyclooctene | $KOC_4H_9$-t | 9,9-Dibromobicyclo[6.1.0]nonane |  | 122 |
| 1,5-Cyclooctadiene | $KOC_4H_9$-t | 9,9,10,10-Tetrabromotricyclo[7.1.0.0$^{4,6}$]decane | 34 | 135 |
| Cyclooctatetraene | $CHBr_3$ | 9,9-Dibromobicyclo[6.1.0]-4 norene | 50 | 95 |
| 1-Ethynylcyclohexene | $KOC_4H_9$-t | 9,9-Dibromobicyclo[6.1.0]-4,6-triene | 72 | 134, 14, 122 |
| Styrene | $CHBr_3$ | 1-Ethynyl-8,6-dibromobicyclo[6.1.0]nona-2,4,6-triene |  | 86, 98 |
| Phenylacetylene | $CHBr_3$ | 1,1-Dibromo-2-phenylcyclopropane |  | 123 |
| Cyclononene | $KOC_4H_9$-t | 1,1-Dibromo-2-phenylcyclopropane |  | 134 |
|  |  | Unidentified |  | 14 |
| 2-Phenyl-1-propene | $CHBr_3$ | 10,10-Dibromotricyclo[7.1.0]decane |  | 14 |
| 3-Phenyl-1-propene | $CHBr_3$ | 1,1-Dibromo-2-methyl-2-phenylcyclopropane | 81 | 134 |
| 1-(p-Methoxyphenyl)-1-propene | $CHBr_3$ | 1,1-Dibromo-2-benzylcyclopropane | 13 | 14 |
| 1-Phenylcyclohexene | $KOC_4H_9$-t | 1,1-Dibromo-2-methyl-3- | 47 | 14 |
|  |  | 1-Phenyl-7,7-dibromobicyclo[4.1.0]heptane |  | 133 |

Note. References 130 to 140 are on p. 90.

* The reactants were heated under reflux in benzene.

TABLE II—*Continued*

REACTIONS OF DIBROMO- AND DIFLUORO-CARBENES WITH ALKENES, ALKYNES, AND CYCLOALKENES

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| 1,9-Cyclotetradecadiene | $CHBr_3$ | $KOC_4H_9$-$t$ | 15,15,16,16-Tetrabromotricyclo[13.1.0.01,14]hexadecane | 22 | 122 |
| Diphenylacetylene | $CHBr_3$ | $KOC_4H_9$-$t$ | Diphenylcyclopropenone† | 28 | 98, 97 |
| Cyclohexene | $CHCl_2F$ | $KOC_4H_9$-$t$ | 7-Chloro-7-fluorobicyclo[4.1.0]heptane | 24 | 57 |
| | $(CH_3)_3SnCF_3$ | ‡ | Perfluorocyclopropane | 95 | 78 |
| | | | Tetrafluoroethylene, fluoroform | — | |
| | $KCF_3BF_3$ | § | Tetrafluoroethylene | 89 | 70 |
| | | | Perfluorocyclobutane, perfluorocyclopropane | Trace | |
| | $KCF_3BF_3$ | ‖ | Perfluorocyclobutane | 90 | 70 |
| | | | Fluoroolefins | | |
| Tetrafluoroethylene | $(CH_3)_3SnCF_3$ | ‡ | Perfluorocyclopropane | 100 | 78 |
| | | | Perfluorocyclobutane | Trace | |
| Cyclohexene | $CHClF_2$ | $KOC_4H_9$-$t$ | Unidentified | — | 57 |
| | $CF_2ClCO_2Na$ | ‡ | 7,7-Difluorobicyclo[4.1.0]heptane | 22 | 65 |
| | | | Carbon dioxide | 60–65 | |

*Note:* References 130 to 140 are on p. 90.

† The product was obtained as the hydrochloride after hydrolysis of the adduct.

‡ Pyrolysis.

§ Pyrolysis at 300° in vacuum.

‖ Pyrolysis at 450° in vacuum.

TABLE III

REACTIONS OF DIHALOCARBENES WITH DOUBLE BONDS IN AROMATIC AND HETEROCYCLIC COMPOUNDS

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Ref. |
|---|---|---|---|---|---|
| Pyrrole | CHCl$_3$ | Pyrrylsodium | 3-Chloropyridine* | | 59 |
| | CHCl$_3$ | Pyrrylpotassium | 3-Chloropyridine | 4 | 59 |
| | CHCl$_3$ | Pyrryllithium | 3-Chloropyridine | 13 | 59 |
| | CHCl$_3$ | 2-Methyl- | 3-Methyl-3-chloropyridine | 7 | 59, 37 |
| | | | | | 37 |
| 2,3-Dihydropyran | CCl$_3$CO$_2$C$_2$H$_5$ | NaOCH$_3$ | 7,7-Dichloro-2-oxabicyclo[4.1.0]heptane | 75 | 119 |
| Benzene | CHCl$_3$ | KOC$_4$H$_9$-t | None | | 60, 99 |
| 2,5-Dimethylpyrrole | CHCl$_3$ | NaOC$_4$H$_9$-t | 3-Chlorolutidine* | 31 | 99 |
| Anisole | CHCl$_3$ | KOC$_4$H$_9$-t | None | | 98 |
| Indene | CHCl$_3$ | Indenylsodium | 2-Chloronaphthalene | 10 | 101 |
| | CHCl$_3$ | | 5-Chloronaphthalene | Trace | |
| 2-Bromoindene | CHCl$_3$ | KOC$_4$H$_9$-t | 1,1-Dichlorocycloprop[a]indene | 65 | 50 |
| 2-Chloroindene | CHBrCl$_2$ | KOC$_4$H$_9$-t | 1,1-Dichlorocycloprop[a]indene | 33 | 57 |
| 2-Methylindole | CHCl$_3$ | KOC$_4$H$_9$-t | Unidentified naphthalene product† | 2 | 89 |
| Skatole | CHCl$_3$ | KOC$_4$H$_9$-t | 1,2-Dichloronaphthalene† | 5 | 89 |
| 2H-1-Benzopyran | CHCl$_3$ | NaOC$_4$H$_9$-t | 3-Chloroquinoline* | | 33 |
| | CCl$_3$CO$_2$C$_2$H$_5$ | NaOCH$_3$ | 3-Chloroquinoline* | | 33 |
| 4H-1-Benzopyran | CHCl$_3$ | NaOCH$_3$ | 1,1-Dichlorocyclopropa[b]benzopyran | 92 | 33 |
| | CCl$_3$CO$_2$C$_2$H$_5$ | NaOCH$_3$ | 1,1-Dichlorocyclopropa[f][1]benzopyran | 24 | 90a |
| | CCl$_3$CO$_2$C$_2$H$_5$ | NaOCH$_3$ | 1,1-Dichlorocyclopropa[b][1]benzopyran | 83 | 90a |
| 4H-1-Benzothiopyran | CHCl$_3$ | NaOCH$_3$ | 1,1-Dichlorocyclopropa[b][1]benzothiopyran | 82 | 90a |
| | CCl$_3$CO$_2$C$_2$H$_5$ | | 1,1-Dichlorocyclopropa[b,l]-benzothiopyran | 24 | 90 |
| 2-Methylindene | CCl$_3$CO$_2$Na | KOC$_4$H$_9$-t | 2-Chloro-3-methylnaphthalene† | 37 | 89 |

Note. References 130 to 140 are cn p. 90.

* The reaction was run in the presence of ethanol

† The product was obtained after treatment with water.

‡ The reactants were heated to reflux in diethylene glycol dimethyl ether

TABLE III—*Continued*

REACTIONS OF DIHALOCARBENES WITH DOUBLE BONDS IN AROMATIC AND HETEROCYCLIC COMPOUNDS

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| 1-Methoxynaphthalene | CCl₃CO₂C₂H₅ | NaOCH₃ | 7-Chloro-2,3-benztropone; Methyl chloride | 11; — | 100 |
| 2-Methoxynaphthalene | CCl₃CO₂C₂H₅ | NaOCH₃ | 7-Chloro-4,5-benztropone | 13 | 100 |
| 1,2,3,4-Tetrahydrocarbazole | CHCl₃ | NaOC₂H₅ | Unidentified product, C₁₃H₁₃Cl₂N | — | 34 |
| 2-Carbethoxyindene | CHCl₃ | KOC₄H₉-t | Unidentified product | — | 89 |
| 9-Methoxyphenanthrene | CCl₃CO₂C₂H₅ | NaOCH₃ | 1,1-Dichloro-1a-methoxy-1H-cyclopropa[1]phenanthrene | 52 | 100 |
| Indene | CHBr₂Cl | KOC₄H₉-t | 2-Chloronaphthalene; 2-Bromonaphthalene | 35; 35 | 57 |
| Pyrrole | CHBr₃ | Pyrryllithium | 3-Bromopyridine | 9 | 59 |
|  | CHBr₃ | Pyrrylsodium | 3-Bromopyridine * | 3 | 59 |
|  | CHBr₃ | Pyrrylpotassium | 3-Bromopyridine | — | 104 |
| Benzene | CHBr₃ | KOC₄H₉-t | None | — | 60 |
| 2,4-Dimethylpyrrole | CHBr₃ | NaOC₂H₅ | 2,5-Dimethyl-3-bromopyridine *; 2,4-Dimethyl-5-bromopyridine | — | 35 |
| 2,5-Dimethylpyrrole | CHBr₃ | NaOC₂H₅ | 3-Bromolutidine * | — | 35 |
| Indene | CHBr₃ | KOC₄H₉-t | 2-Bromonaphthalene † | 52 | 50 |
| 2-Methylindole | CHBr₃ | NaOC₂H₅ | 3-Bromoquinaldine * | — | 33 |
| Skatole | CHBr₃ | NaOC₂H₅ | 3-Bromolepidine * | — | 33 |
| 1-Methylindene | CHBr₃ | KOC₄H₉-t | 1-Methyl-2-bromonaphthalene | 44 | 50 |
| 2-Methyl-5-phenylpyrrole | CHBr₃ | NaOC₂H₅ | Unidentified pyridine base * | Trace | 35 |
| Indole | CHI₃ | KOC₄H₉-t | None | — | 33 |

*Note:* References 130 to 140 are on p. 90.

* The reaction was run in the presence of ethanol.

† The product was obtained after treatment with water.

TABLE IV

REACTIONS OF DIHALOCARBENES WITH MISCELLANEOUS UNSATURATED COMPOUNDS

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| Allyl chloride | CCl₃CO₂Na |  | 1,1-Dichloro-2 chloromethylcyclopropane | 60 | 66 |
| Ethyl vinyl ether | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2-ethoxycyclopropane |  | 65 |
| Divinyl ether | CHCl₃ | KOC₄H₉ᵗ | Bis (2,2-dichlorocyclopropyl) ether | 16 | 139 |
| Vinyl acetates | CCl₃CO₂C₄H₉, CCl₃CO₂Na | Na₂CO₃ | 1,1-Dichloro-2 acetoxy-n. propane | 10 | 139 |
| Ketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 dimethoxycyclopropane | 4 | 68 |
| Hexachlorobutadiene | CHCl₃ | KOC₄H₉ᵗ | None |  | 128 |
| Methylketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 dimethoxy-3 methylcyclopropane | 52 | 128 |
| Ketene diethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 diethoxycyclopropane | 68 | 128 |
| Dimethylketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 dimethoxy-3,3 dimethylcyclopropane | 61 | 128 |
| Ethylketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 dimethoxy-3 ethylcyclopropane | 56 | 128 |
| n-Propylketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | 1,1-Dichloro-2,2 dimethoxy-3-n propylcyclopropane | 35 | 128 |
| Di-isopropenyl ether | CHBr₃ | NaOCH₃ | Bis (2,2-dibromo 3,3 dimethylcyclopropyl) ether | 20 | 139 |
|  | CHBr₃, CCl₃CO₂C₄H₉ | KOC₄H₉ᵗ, NaOCH₃ | Bis (2,3-dibromo-3,3 dimethylcyclopropyl) ether | 26 | 139 |
| 2H-1-Benzothiopyran | CHBr₃ | KOC₄H₉ᵗ | 2 Dibromomethyl 2H-1 benzothiopyran | 22 | 90 |
|  |  |  | 4 Dichloromethyl 4H-1 benzothiopyran | 9 |  |
|  |  |  | Unidentified diadduct, C₁₁H₁₀Cl₄S | 8 |  |
|  | CCl₃CO₂Na |  | 2 Dibromomethyl 2H-1 benzothiopyran | 15† |  |
|  |  |  | 2 Dichloromethyl 4H-1 benzothiopyran | 13 |  |
| Phenylketene dimethylacetal | CHCl₃ | KOC₄H₉ᵗ | Dimethyl t-butyl orthophenylpyruvate | 20 | 90 |
|  |  |  | Methyl phenylpropiolate | 20 | 128 |
|  |  |  | Methyl phenylacetate | 50 |  |
| Benzalaniline | CHCl₃ | NaOCH₃ | 2,2 Dichloro-1,3 diphenylethylenimine | 45 | 167 |
|  | (CCl₃)₂CO | NaOCH₃ | 2,2 Dichloro-1,3 diphenylethylenimine | 61 | 64 |

Note   References 120 to 140 are on p. 90.
* The substance reacts at reflux in diethylene glycol dimethyl ether.
† The yields of the products were estimated from nuclear magnetic resonance spectral data.

TABLE V

REACTIONS OF MONOHALOCARBENES

| Carbene Acceptor | Carbene Precursor | Base | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| 2-Methylpropene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-2,2-dimethylcyclopropane | 44 | 83 |
|  | $CH_2Cl_2$ | $CH_3Li$ | 1-Chloro-2,2-dimethylcyclopropane | 50 | 83 |
| cis-2-Butene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-cis-2,3-dimethylcyclopropane (the cis/trans chlorine ratio was 1:5.5) | 30 | 83 |
| trans-2-Butene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-trans-2,3-dimethylcyclopropane | 40 | 83, 10 |
| Pyrrole | $CH_2Cl_2$ | $CH_3Li$ | Pyridine | 32 | 106 |
| 1,2-Dimethylpropenyllithium | $CH_2Cl_2$ | $CH_3Li$ | 1,3,3-Trimethylcyclopropene* | 40–50 | 140 |
| 2-Methyl-2-butene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-2,2,3-trimethylcyclopropane (the cis/trans ratio was 1:1.6) | 50 | 83 |
| 1-Pentene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-2-n-propylcyclopropane (the cis/trans ratio at −35°, 1:3.4) | 10 | 83 |
| Dihydropyran | $CH_2Cl_2$ | $CH_3Li$ | 1-Chloro-2-n-propylcyclopropane (the cis/trans ratio at 30°, 1:1.8) | 25 | 83 |
|  | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 7-Chloro-2-oxabicyclo[4.1.0]heptane (the exo/endo ratio was 3.2:1) | 28 | 119 |
| 2,3-Dimethyl-2-butene | $CH_2Cl_2$ | $n$-$C_4H_9Li$ | 1-Chloro-2,2,3,4-tetramethylcyclopropane | 67 | 83, 10 |

| Reactant | Dihalide | Base | Product | Yield | Ref. |
|---|---|---|---|---|---|
| Cyclohexene | $CH_2Cl_2$ | $n\text{-}C_4H_9Li$ | 7-Chlorobicyclo[4.1.0]heptane (the exo/endo ratio was 2.2:1) | 31 | 10 |
| Benzene | $CH_2Cl_2$ | $CH_3Li$ | 7-Bromobicyclo[4.1.0]heptane (the exo/endo ratio was 3.2:1) | 48 | 83 |
| | $CH_2Cl_2$ | $CH_3Li$ | Methylcycloheptatriene | 20 | 99 |
| | | | Ethylene | — | 60 |
| Lithium phenoxide | $CH_2Cl_2$ | $KOC_4H_9$ / $CH_3Li$ | t-Butoxycycloheptatriene† | 2 | 103 |
| | $CH_2Cl_2$ | $CH_3Li$ | Tropone | 0.2 | |
| | | | 2-Methyl-3,5-cycloheptadienone* | 44 | 103 |
| Lithium o-cresyloxide | $CH_2Cl_2$ | $CH_3Li$ | Methyltropylium chloroplatinate‡ | 4 | 106 |
| | | | 2,7-Dimethyl 3,5-cycloheptadienone | 23 | 103 |
| | | | 1,2-Dimethyltropylium chloride‡ | 3 | 60 |
| Indole | $CH_2Cl_2$ | $CH_3Li$ | Quinoline | 13 | |
| 2,6-Di-t-butylphenoxide | $CH_2Cl_2$ | $CH_3Li$ | 2,7-Di-t-butyltropone | 70 | |
| | | | t-Butoxytropylium chloride‡ | 1 | |
| Benzene | $CH_2Br_2$ | $CH_3Li$ | t-Butoxycycloheptatriene† | Trace | 59, 61 |
| Pyrrole | $CH_2I_2$ | $NaOC_4H_9$ / $NaOCH_3$ | Pyridine | 0.1 | 60 |
| Benzene | $CH_2I_2$ | $KOC_4H_9$ | t-Butoxycycloheptatriene† | | |

*Note.* References 130 to 140 are on p. 90.

* The intermediate 2,3,3-trimethylcyclopropenyllithium was isolated as the product listed.

† The product was isolated as the tropylium bromide after treatment with hydrogen bromide.

‡ The product was isolated after acidification.

## REFERENCES FOR TABLES I–V

[130] Ter Borg and Bickel, *Rec. Trav. Chim.*, **80**, 1217 (1961); *Proc. Chem. Soc.*, **1958**, 283.

[131] Wawzonek and Duty, *J. Electrochem. Soc.*, **108**, 1135 (1961).

[132] Hauser, Kofron, Dunnavant, and Owens, *J. Org. Chem.*, **26**, 2627 (1961).

[133] Petrov, Nefedov, and Kolesnikov, *Zhur. Vses. Khim. Obshchestva im. D. I. Mendeleeva,* [4] **6**, 471 (1961) [*Index Chemicus*, **1961**, 13116].

[134] Dale and Swartzentruber, *J. Org. Chem.*, **24**, 955 (1959).

[135] Vogel, *Angew. Chem.*, **73**, 548 (1961).

[135a] Sonnenberg and Winstein, *J. Org. Chem.*, **27**, 748 (1962).

[136] Hofmann, Orochena, Sax, and Jeffrey, *J. Am. Chem. Soc.*, **81**, 992 (1959).

[137] Hofmann, Orochena, and Yoho, *J. Am. Chem. Soc.*, **79**, 3608 (1957).

[138] Vogel, Ott, and Gajek, *Ann.*, **644**, 172 (1961).

[139] Gillis and Schimmel, *J. Org. Chem.*, **27**, 1071 (1962).

[140] Closs and Closs, *J. Am. Chem. Soc.*, **83**, 2015 (1961).

# CHAPTER 3

## FREE RADICAL ADDITIONS TO OLEFINS TO FORM CARBON-CARBON BONDS

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## CONTENTS

# INTRODUCTION

Some of the most useful reactions in synthetic organic chemistry involve the addition of reagents across the double bonds of olefins. These reactions, which can occur by a variety of mechanisms involving electrophilic, nucleophilic, or radical intermediates, have been the subject of numerous mechanistic studies. Electrophilic additions involve polar reagents, and in general the direction of addition follows Markownikoff's rule. Nucleophilic additions require rather special and drastic conditions unless the olefin contains strong electron-withdrawing substituents. Radical reactions are very general in scope but are markedly influenced by light, oxygen, peroxides, and various inhibitors.

The direction of addition in the free radical reaction is commonly the opposite of that encountered in the electrophilic ionic (Markownikoff) additions. Hence these free radical additions have been referred to as

anti-Markownikoff, abnormal, or, more recently, Kharasch addition reactions. This chapter is concerned with the synthetic aspects of Kharasch addition reactions that result in the formation of a new carbon-carbon bond

The discovery that certain compounds could add to olefins in a free radical chain reaction was made in the nineteen-thirties  The presently accepted mechanism of the anti-Markownikoff addition of hydrogen bromide and mercaptans was suggested by Kharasch in 1937,[1] and

TABLE I

| Class | Products |
|---|---|
| Polyhalomethanes | Halogenated hydrocarbons |
| Aldehydes | Ketones |
| Alcohols | |
| Primary | Secondary alcohols |
| Secondary | Tertiary alcohols |
| Methanol | Primary alcohols |
| Amines | Amines alkylated on the α-carbon atom |
| Esters (and other acid derivatives) | α-Alkyl esters (and other acid derivatives) |
| Formate esters | Monocarboxylic esters |
| Ethers | Ethers alkylated on the α-carbon atom |

independently by Waters[2] in the same year. The first examples of a simple addition reaction resulting in the formation of a new carbon-carbon bond were given in 1945 by Kharasch, who reported that carbon tetrachloride and chloroform reacted with 1-octene to form 1,1,1,3 tetrachlorononane and 1,1,1-trichlorononane, respectively.[3]

It had previously been noted that carbon tetrachloride had a marked effect in lowering the degree of polymerization of styrene, an observation explained quantitatively by Mayo in 1943 in terms of a chain transfer process[4]  Also prior to the Kharasch publication, the addition of carbon tetrachloride to olefins to form products of low molecular weight had been observed independently by research groups at the du Pont and U S. Rubber companies[5]  Since this time, a number of other compounds have been found to add to olefins in a free radical chain reaction  In Table I, those classes of compounds which on addition to an alkene result

[1] Kharasch, Engelmann, and Mayo, J. Org Chem, 2, 288 (1937).
[2] Hey and Waters, Chem Revs, 21, 169 (1937).
[3] Kharasch, Jensen, and Urry, Science, 102, 128 (1945).
[4] Mayo, J. Am. Chem Soc, 65, 2324 (1943)
[5] Walling, Free Radicals in Solution, p 247, John Wiley and Sons, Inc, New York, 1957.

in the formation of a new carbon-carbon bond are listed along with the resulting addition products.

Although the majority of these Kharasch additions have been performed with alkenes as the unsaturated species, many other unsaturated compounds, e.g., vinyl acetate, maleate esters, allyl halides, have been used with success and have led to the formation of di- or poly-functional addition products. Additions to simple olefins and to olefins containing other functional groups are included in the Tabular Survey.

## MECHANISM

### Characteristics of Radical Chain Reactions

Because the addition reactions discussed in this chapter are typical radical chain reactions, some comments on such processes are in order. The over-all reaction in which a molecule A—B is added across a double bond in the presence, for example, of a peroxidic initiator actually occurs through a complex sequence of steps involving transient free radicals as intermediates. These steps may be indicated as follows.

$$A—B + CH_2=CHR \xrightarrow{ROOR} CH_2ACHBR \qquad (1)$$
$$ROOR \rightarrow 2RO\cdot \qquad (2)$$
$$RO\cdot + AB \rightarrow ROB + A\cdot \qquad (3)$$
$$A\cdot + CH_2=CHR \rightarrow ACH_2\dot{C}HR \qquad (4)$$
$$ACH_2\dot{C}HR + AB \rightarrow ACH_2CHBR + A\cdot \qquad (5)$$
$$2A\cdot \rightarrow A—A \qquad (6)$$
$$2ACH_2\dot{C}HR \rightarrow ACH_2CH(R)CH(R)CH_2A \qquad (7)$$
$$A\cdot + ACH_2\dot{C}HR \rightarrow ACH_2CHAR \qquad (8)$$
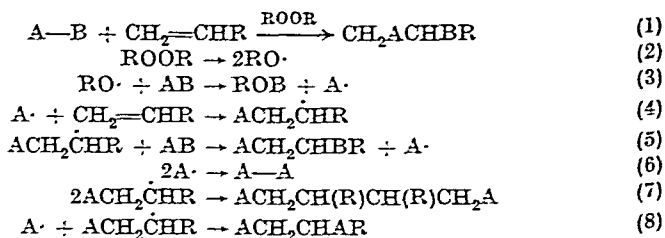
In such a scheme steps (2) and (3) represent chain initiation, (6) to (8) chain termination, and (4) and (5) chain propagation.

The reactions represented by equations 4 and 5 are the important steps in determining the products since the radical A· consumed in (4) in an addition reaction is regenerated in (5), a radical displacement reaction, and many (often hundreds or thousands) of such cycles may occur for every radical introduced into the system. In contrast, since chain termination steps destroy radicals, no more termination products are produced than chains are started; they contribute little to the reaction, and the over-all stoichiometry of the process (in the absence of side reactions which involve alternative chain propagation steps) is essentially that of reaction 1. On the other hand, the *over-all reaction rate* and the *kinetic chain length* (or molecules of product produced per molecule of initiator starting chains) which essentially determine the *yield* under a given set of experimental conditions depend on each of the three processes of initiation, propagation,

and termination   The rate of initiation of chains can in general be controlled by suitable choice of initiator, temperature, and other experimental conditions   The rate of chain termination is subject to no such direct control and imposes a very serious limitation on the scope of chain processes   Bimolecular reactions between radicals such as (6) to (8) almost invariably have very high rate constants ($\sim 10^7$ l/mole/sec.), with the consequence that the time interval between the initiation and termination of a chain is only of the order of a second.   If a large number of chain propagation steps are to be interposed into such a short time interval, it is evident first that they must be very rapid, low activation energy processes and, second, that small changes in structure of the addend AB or olefin may have large effects on over-all rates and yields.

The effect of changes of structure on reactivity in radical reactions can be treated quite successfully in terms of resonance, steric, and polar phenomena (pp. 95–99)   When due allowance is made for the side reactions discussed below, these factors permit a satisfactory semiquantitative picture of radical addition reactions even though relatively few detailed kinetic studies of such systems have been published.

Lewis and Mayo have investigated the effect of olefin/addend ratio on yields in a number of halomethane additions with results which appear to be quite general.[6]   At low olefin/addend ratios, reaction 4 becomes the slow step in propagation, radical A· accumulates in the system, and chain termination occurs through (6), with the kinetic consequence that the over-all reaction is first-order in olefin   At high olefin/addend ratios, (5) is the slow propagation step, termination occurs through (7), and the over-all reaction is first-order in addend   At intermediate ratios, termination may involve both (6) and (7) and also (8), but the general result is a rather pronounced maximum in rate (or yield with a given amount of initiator) at some particular olefin/addend ratio   Some typical yield curves are shown in Fig 1 and support this conclusion.   They also illustrate the profound sensitivity of these addition reactions to small changes in structure to which we now turn our attention

## Structure and Reactivity

The over-all addition reaction 1, where A· is a hydrocarbon radical, is in general exothermic by about 20 kcal/mole.   However, if both propagation steps (4) and (5) are to be rapid, low activation energy processes, this energy must be suitably divided between the two, or in any case the balance should not be so poor that one is significantly endothermic   The manner in which this division occurs is determined primarily by the

[6] Lewis and Mayo, J. Am Chem Soc, 76, 457 (1954)
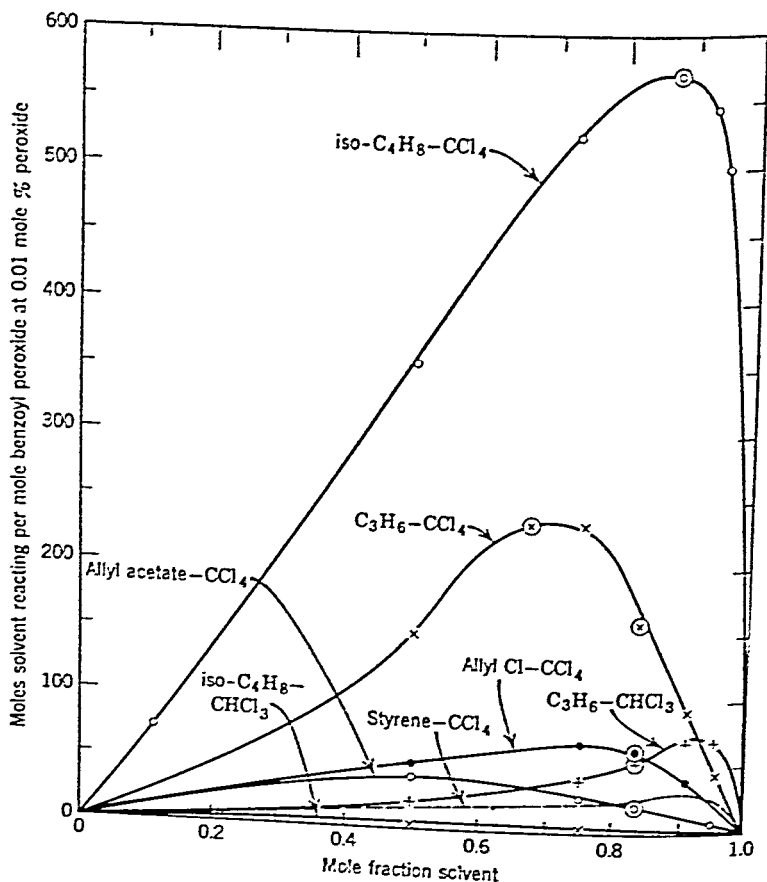
FIG. 1. Variation in yield with solvent/olefin ratio in radical addition of halomethanes to olefins. From C. Walling, *Free Radicals in Solution*, John Wiley and Sons. Inc., New York, 1957, p. 260.
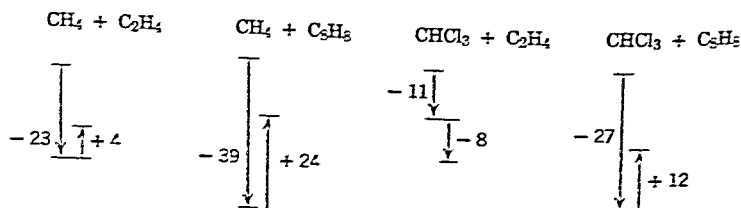


FIG. 2. Energetics of addition of $CH_4$ and $CHCl_3$ to ethylene and styrene. in kilo-calories per mole. First arrow for reaction (4), second for reaction (5). Data assume $\Delta H_{(overall)} = -19$ kcal. for ethylene additions and $-15$ kcal. for styrene.

effective resonance energies of the radicals A· and R· involved in the two steps.* This resonance energy can be deduced from bond dissociation energy data, and typical values appear in Table II; the methyl radical, $CH_3$·, is taken as a standard for comparison. Since in reaction (4) the resonance energy of A· is lost and that of R· is gained, a highly stabilized A· radical will decrease the exothermicity of the process, while substituents on the olefin leading to a highly stabilized radical R· will increase the exothermicity. In reaction (5) the resonance energy of $ACH_2CHR$ is lost while that of A· is gained, and the opposite situation results. As examples,

TABLE II

BOND DISSOCIATION ENERGIES AND RESONANCE ENERGIES OF FREE RADICALS

| Bond | $\Delta H_0$ D(R—H), kcal/mole | Resonance Energy of Radical, kcal/mole |
|---|---|---|
| H—$CH_3$ | 102 | 0 |
| H—$C_2H_5$ | 98 | 4 |
| H—$CH_2CH_2CH_3$ | 100 | 2 |
| H—$CH(CH_3)_2$ | 94 | 8 |
| H—$C(CH_3)_3$ | 90 | 12 |
| H—$CH_2CH=CH_2$ | 77 | 25 |
| H—$CH_2C_6H_5$ | 77.5 | 24.5 |
| H—$C(CH_3)_2CO_2CH_3$ | $(75)^a$ | 27 |
| H—$CCl_3$ | 90 | 12 |
| Cl—$CCl_3$ | 68 | 12 |
| Br—$CCl_3$ | 49 | 12 |
| I—$CCl_3$ | $(39)^a$ | 12 |

$^a$ This value has a larger uncertainty than those not in parentheses. See reference 5, pp. 47–49.

Fig 2 illustrates the calculated energetics of addition of methane and chloroform (as $CH_3$—H and $CCl_3$—H) to ethylene and to styrene. Here ·$CCl_3$ and the radical R· from styrene are stabilized by approximately 12 and 24 kcal/mole, respectively. Replacing $CH_3$· by $CCl_3$· decreases the exothermicity of reaction (4) and increases that of (5). On the other hand, replacing $CH_3$· by styrene increases the exothermicity of (4) and decreases that of (5). Only in the chloroform-ethylene system are both steps exothermic, and this is also the only one of the four reactions which has been observed as a long-chain process giving a simple 1.1 adduct. Similar approximate calculations can be made for other systems by correcting the basic energetics of the methane ethylene reaction by the resonance stabilization values given in Table II.

* Resonance stabilization of the double bond also plays a minor role in the division but is not taken into account in this brief discussion.

In a series of addends A—B in which the carbon radical A· is held constant and B is changed, reactivity generally increases in the sequence $H < Cl < Br < I$. Thus $CCl_3$—Br undergoes addition more readily than $CCl_3$—Cl, and $CF_3$—I more readily than $CF_3$—Br. The differentiation between Cl— and H— is less clear-cut and depends to some extent on the particular system involved. Thus chloroform is usually less reactive than carbon tetrachloride and adds as $CCl_3$—H. Bromoform is more reactive and adds as $CHBr_2$—Br. On the other hand, aldehydes add as RCO—H, while acid chlorides fail to give a comparable addition as RCO—Cl. No displacement involving fluorine is known, and, although displacements involving other atoms attached to carbon have been observed, they do not in general lead to carbon-carbon bond formation and accordingly are outside the scope of this chapter.

Although it is advantageous for the radical reactions to be exothermic, this is not solely sufficient to provide for fast radical chains. Even strongly exothermic processes may have significant activation energies, and small differences in activation energies (or in pre-exponential factors) may lead to large differences in rate. These more subtle effects of structure have been studied in detail, chiefly by the use of competitive reactions, and can be discussed in terms of steric and polar factors.

Steric hindrance affects radical reactions, particularly in the addition step (4). Thus non-terminal olefins generally undergo addition reactions less readily than terminal olefins and give lower yields of the desired products. In fact, the usual direction of addition in radical reactions, in which the radical A· adds to the less-substituted end of the double bond, is probably largely a steric effect, although it is also aided by the greater resonance stabilization of the resulting radical. Steric hindrance in the displacement step (5) seems to be less important and, in fact, is not well established.

Another factor which plays a very important role in the rates of both radical displacements and additions appears to be polar in nature: radicals with strong electron-withdrawing groups show enhanced reactivity with substrates bearing electron-supplying groups, and vice versa. The nature of this polar effect has received considerable discussion and appears to vary from a simple dipolar interaction to, in extreme cases, the lowering of the energy of the transition state by contributions from charge transfer structures. We may note that radicals with electron-withdrawing groups that have corresponding negative ions of reasonable stability add with particular facility to olefins of high electron availability, while radicals with stable corresponding carbonium ions add well to olefins bearing electron-withdrawing groups. Thus polyhalomethanes react readily with hydrocarbons, vinyl ethers, etc., while aldehydes and alcohols

(which add as RCHOH—H) give particularly good yields of adducts with perfluoroolefins and $\alpha,\beta$ unsaturated carbonyl compounds such as maleate esters  The reality of these polar effects has been amply demonstrated by the study of competitive reactions, and the effects appear to be as important as the other factors mentioned above in determining the success or failure of a given reaction *

## Telomer Formation

The radical addition described by the reaction sequence (2-8) may be subject to competing processes which interfere with the desired chain  The most important is polymerization  Actually, reaction (5) is always in competition with addition of the olefin-derived radical to another molecule of olefin  The result is that, besides the simple addition product,

$$
ACH_2CHBr \xrightarrow{\ AB\ (k_d)\ } ACH_2CHBr - A \qquad \xrightarrow{\ AB\ } ACH_2CHRCH_2CHBr + A\cdot
$$

$$
ACH_2CHr \qquad\qquad\qquad\qquad\qquad \tag{9}
$$

$$
\xrightarrow{\ CH_2=CHR\ (k_a)\ } ACH_2CHRCH\cdot CHR \xrightarrow{\ CH_2=CHR\ } \text{etc.}
$$
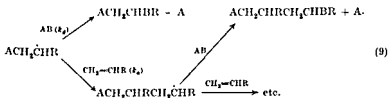
$ACH_2CHBR$, a series of higher products, $A(CH_2CHR)_nCH_2CHBR$, may be produced as well  These materials, known as telomers, are usually undesired by-products because they have rather complex branched structures  However, in the case of ethylene and tetrafluoroethylene, telomerization provides a powerful synthetic method for the preparation of long-chain molecules $A(CH_2CH_2)_nB$ and $A(CF_2CF_2)_nB$.

The importance of telomer formation can be assessed quantitatively in terms of the constant $C$, the ratio of the rate constants for reaction of an olefin derived radical $R\cdot$ with AB and with another molecule of olefin  A simple kinetic analysis shows that, in reaction (9),

$$
\frac{\text{mole fraction 1:1 product}}{\text{mole fraction telomers}} = \frac{k_d[AB]}{k_a[\text{olefin}]} = C_1\frac{[AB]}{[\text{olefin}]} \tag{10}
$$

where $C_1$ is the first transfer involving the reaction of $R\cdot$ containing just one olefin unit  In the same manner, the expression may be generalized

$$
\frac{\text{mole fraction } N:1 \text{ product}}{\text{mole fraction higher products}} = C_N\frac{[AB]}{[\text{olefin}]} \tag{11}
$$

* For a further discussion of these effects see reference 5, pp. 132–140

The resulting distribution functions have been worked out so that the entire product distribution can be calculated for systems in which the transfer constants are known.*

With $C > 1$, high yields of 1:1 products can be obtained with a small excess of AB. In principle, good yields can also be obtained in systems where $C \ll 1$ by working at very high ratios of [AB]/[olefin], or by adding

TABLE III

VARIATION OF TRANSFER CONSTANTS FOR POLYHALOMETHANES
WITH CHAIN LENGTH[7]

| System | $C_1$ | $C_2$ | $C_n$ |
|---|---|---|---|
| Ethylene-CCl$_4$ (70°) | 0.08 | 1.9 | 3.2[a] |
| Propylene-CCl$_4$ (100°) | 1.3 | | 5–10 |
| Propylene-CHCl$_3$ (100°) | 0.11 ± 0.01 | 0.55 ± 0.03 | 1.03 ± 0.05 |
| Isobutylene-CCl$_4$ (100°) | 1.4 ± 0.4 | | 17 ± 3 |
| Allyl chloride-CCl$_4$ (100°) | 0.01 − 0.02 | 0.10 ± 0.05 | 0.48 ± 0.03 |
| Allyl acetate-CCl$_4$ (100°) | 0.01 ± 0.01 | 0.5 ± 0.2 | 2.0 ± 1.0 |
| Styrene-CCl$_4$ (76°) | 0.0006 | 0.0025 | 0.0115[b] |

[a] This is the value for $C_3$.
[b] The value for $C_3$ is 0.004.

the olefin slowly during the reaction, although kinetic chains may be short under these conditions, thus requiring a relatively large amount of initiator. Since small transfer constants generally increase with temperature, better yields of 1:1 product may also be obtained at higher temperatures.

Optimizing the yield of a telomer containing a particular number of olefin units is a more complicated matter. The yield of any particular telomer is dependent on the addend/olefin ratio and passes through a maximum value at a particular addend/olefin ratio. The situation is helped somewhat by the fact that transfer constants frequently increase significantly until $n = 3$ or 4, so that quite good yields of 2:1 or 3:1 products can be obtained. Some typical values are listed in Table III.

Transfer constants vary with structure in the manner suggested by the previous discussion. In the addend A—B, they increase with changes in B from H < Cl < Br < I, and with substituents in A that increase its resonance stabilization, since all these changes increase the rate of the displacement reaction. Thus bromotrichloromethane gives good yields of 1:1 products in reactions with equimolecular quantities of most olefins, while carbon tetrachloride must be used at high carbon tetrachloride/olefin ratios. Polyhalomethanes with less than three halogens generally give

* See Ref. 5, chap. 6.
[7] Ref. 5, p. 257.

low yields of 1 1 products unless the methanes are further activated by nitrile, carbonyl, or similar groups

The situation with olefins is slightly more complicated. Substituents stabilizing R· also increase olefin reactivity, so the tendency to add another olefin does not change greatly with structure. On the other hand, resonance stabilization of R· decreases the rate of the displacement reaction, so telomer formation is favored. Thus ethylene, vinyl acetate, and other olefins which polymerize will alone but react via highly reactive, unstabilized radicals give 1·1 products in many systems. In contrast, styrene and methyl acrylate usually give only telomers of high molecular weight. Non-terminal olefins, in which polymerization is retarded by steric hindrance, show little tendency to form telomeric products, although the desired 1:1 addition may not occur in high yield

Finally, polar effects may again play a decisive role in the competition of reaction (9), as well as in the rate of the over-all addition reaction. As examples, perfluoroolefins have high transfer constants with alcohols and give good yields of 1 1 products with alcohols, in contrast to non-fluorinated olefins such as ethylene.

## Allylic Attack

A second complication in radical addition processes arises from the possibility of competition between the desired addition (4) and displacement reactions between the radical A· and the olefin. Here attack upon allylic hydrogen atoms is particularly likely because of the high resonance stabilization of the resulting allylic radical,

$$A· + CH_2{=}CHCH_2R$$

$$\begin{array}{c} \nearrow^{k_a} \quad CH_2{=}CHCHR + AH \\ \\ \searrow^{k_b} \quad ACH_2CHCH_2R \end{array} \qquad (12)$$
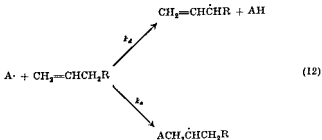
and the importance of the reaction depends obviously on the ratio of rate constants $k_a/k_b$ in equation 12. The role of such a side reaction in polymerization was first pointed out by Bartlett and Altschul,[8] and its importance in radical additions by Israelashvili and Shabatay[9]

[8] Bartlett and Altschul, J. Am Chem Soc, 67, 816 (1945).

[9] Israelashvili and Shabatay, J. Chem. Soc., 1951, 3261

The few available estimates of the values of $k_d/k_a$ ratios give an idea of the amount of side reaction to be expected. For the reaction of methyl radicals with isobutylene at 65°, $k_d/k_a = 0.06$, and increases to 0.95 and 0.7 for *cis-* and *trans*-2-butene, presumably because of the decreased rate of addition to a non-terminal double bond.[10] When A· is a more highly resonance-stabilized radical, the amount of allylic attack is decreased. The situation with the $CCl_3$· radical has been studied in some detail.[11,12] For 1-hexadecene, $k_d/k_a$ is 0.018, while for cyclohexene it is approximately 0.5. The data in Table IV illustrate the influence of some structural

TABLE IV

RELATIVE AMOUNTS OF HYDROGEN ABSTRACTION AND ADDITION
BY THE TRICHLOROMETHYL RADICAL WITH VARIOUS OLEFINS[12]

| Olefin | Temperature, °C. | $k_d/k_a$ |
|---|---|---|
| *cis*-2-Butene | 99.0 | 0.029 |
| *trans*-2-Butene | 99.0 | 0.038 |
| 2-Pentene | 77.8 | 0.18 |
| Cyclopentene | 77.8 | 0.18 |
| | 40.0 | 0.54 |
| 4-Methyl-2-pentene | 77.8 | 0.81 |
| | 40.0 | 0.60 |
| Cyclohexene | 77.8 | 0.83 |
| | 40.0 | 0.54 |
| 3-Heptene | 77.8 | 0.29 |
| | 40.0 | 0.20 |
| Cycloheptene | 77.8 | 0.18 |
| | 40.0 | 0.12 |
| 1-Octene | 77.8 | 0.023 |
| 1-Decene | 77.8 | 0.023 |

features of the olefin on the amount of allylic attack. Terminal olefins, with double bonds that are very reactive toward addition, suffer comparatively little allylic attack in comparison to non-terminal olefins. Furthermore, non-terminal olefins with very reactive allylic hydrogen atoms, such as the tertiary allylic hydrogen atom in 4-methyl-2-pentene and the ring hydrogen atoms in cyclohexene, suffer a considerable amount of allylic attack.

Allylic attack is a complication in addition reactions, not only because it introduces a competing side reaction, but also because it may lead to the termination of kinetic chains with a resulting reduction of over-all

[10] Buckley, Leavitt, and Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956).

[11] Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).

[12] Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

product yield. Since the resulting allylic radical is a highly resonance-stabilized species, it may fail to react with the addend A—B and instead accumulate in the system until it disappears by bimolecular coupling or disproportionation reactions. This difficulty shows up very plainly in addition reactions to cyclohexene. Carbon tetrachloride gives only low yields of any product, while bromotrichloromethane gives a rapid reaction with long kinetic chains. Here the allylic radicals re-enter the chain by the sequence

$$\text{[cyclohexene]}\cdot + CCl_3Br \rightarrow \text{[bromocyclohexene]}Br + CCl_3 \qquad (13)$$
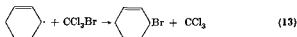
and, from the value of $k_d/k_a$ given, about a third of the olefin that reacts would be converted to 3-bromocyclohexene and about two-thirds to the addition product 1-trichloromethyl-2-bromocyclohexane.

More detailed discussions of the kinetic significance of allylic attack are available.[5],[11],[13]

## Rearrangements

The rearrangements that sometimes accompany radical additions may be classified in three types: 1,2 shifts, ring opening and closure, and a miscellaneous group. A more detailed discussion of radical rearrangements in general is given elsewhere.[14]

In radical processes 1,2 shifts of neighboring groups are much less common than in processes involving carbonium ions, and unequivocal examples appear to be restricted to the migration of an aryl group or a halogen atom.

The only reported example of aryl migration in a radical addition is in the addition of *n*-butyraldehyde to 3,3-diphenyl-1-butene which gives propyl 2,3-diphenylbutyl ketone,[15] presumably by the sequence shown. Similar rearrangements might be expected in comparable systems, but have not been investigated.

$$\overset{\text{O}}{\underset{\text{RC}}{\parallel}} + CH_2{=}CHCCH_3 \overset{C_6H_5}{\underset{C_6H_5}{\mid}} \longrightarrow \overset{\text{O}}{\underset{\text{RCCH}_2CHCCH_3}{\parallel}} \overset{C_6H_5}{\underset{C_6H_5}{\mid}} \qquad (14)$$
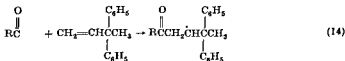
13 Kooyman and Farenhorst, Rec Trav Chim , 70, 867 (1951)

14 Walling, "Free Radical Rearrangements," in P DeMayo, *Molecular Rearrangements*, Interscience, New York, in press

15 Weinstock and Lewis, J. Am. Chem. Soc , 79, 6243 (1957)

$$R-\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H\overset{\cdot}{C}CH_3 \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\cdot}{C}}CH_3 \quad (15)$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\cdot}{C}}CH_3 + RCHO \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H-\overset{\overset{\displaystyle C_6H_5}{|}}{C}HCH_3 + R-\overset{\overset{\displaystyle O}{\|}}{\underset{\cdot}{C}} \quad (16)$$
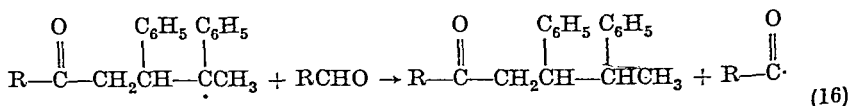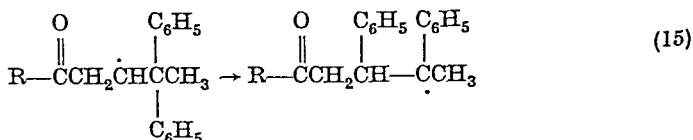
As an example of halogen migration, the addition of bromotrichloromethane to 3,3,3-trichloropropene gives a complex mixture of products (A, B, and C) which seems to require halogen migration as indicated.[16]

$$CH_2\!\!=\!\!CHCCl_3 + \cdot CCl_3 \rightarrow$$

$$CCl_3CH_2\overset{\cdot}{C}HCCl_3 \rightarrow CCl_3CH_2CHCl\overset{\cdot}{C}Cl_2 \xrightarrow{CCl_3Br} CCl_3CH_2CHClCCl_2Br$$
$$(A)$$
$$\downarrow$$
$$\swarrow CCl_3CH_2CH\!\!=\!\!CCl_2 + Cl\cdot$$
$$(B) \qquad\qquad (17)$$

$$Cl\cdot + CH_2\!\!=\!\!CHCCl_3 \rightarrow CCl_3\overset{\cdot}{C}HCH_2Cl \xrightarrow{CCl_3Br}$$
$$CCl_2BrCHClCH_2Cl \quad \text{or} \quad CCl_3CHBrCH_2Cl$$
$$(C)$$
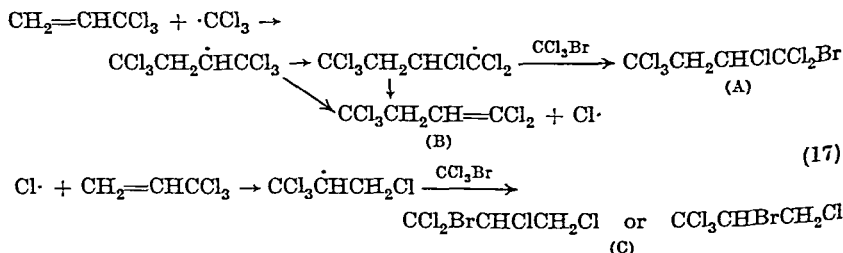
Since the structure of C was not unequivocally determined, occurrence of the second rearrangement remains in doubt.

Ring-opening reactions may take place in highly strained systems and are exemplified by the addition of carbon tetrachloride to α-pinene.[17]



$$(18)$$
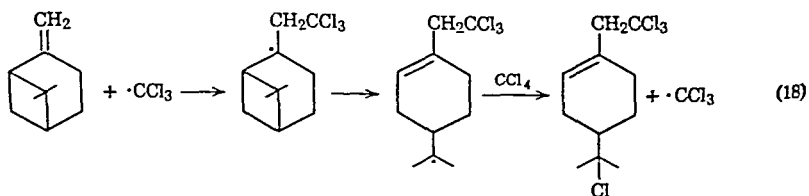
Similar products result from the addition of other carbon radicals, although with mercaptan additions where the displacement step is very rapid no ring opening occurs.

[16] Nesmeyanov, Freidlina, and Zakharin, *Doklady Akad. Nauk USSR*, **81**, 199 (1951) [*C.A.*, **47**, 3789 (1953)].

[17] Oldroyd, Fisher, and Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950).

*Ring closures*, essentially the reverse of sequence (*18*), are also possible in additions to suitable dienes. Thus the reaction of carbon tetrachloride with diallyl ether follows the sequence shown.[18]



(19)
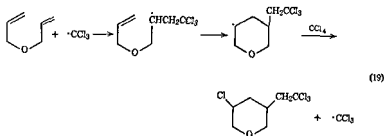
Similar processes have been reported. A tricyclene derivative is the predominant 1:1 addition product obtained in the reaction of bromotrichloromethane with 5-methylenebicyclo[2.2 1]hept-2-ene.[19]



(20)
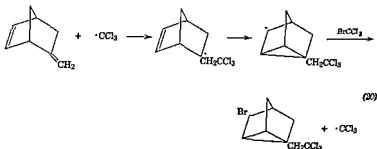
Finally, additions are sometimes complicated by side reactions involving loss of halogen from intermediate radicals. Reaction sequence (*17*) provides an example, as does the addition of bromotrichloromethane to allyl bromide which yields D, E, and F.[20]

$$\cdot CCl_3 + CH_2=CHCH_2Br \longrightarrow CCl_3CH_2\dot{C}HCH_2Br \longrightarrow CCl_3CH_2CH=CH_2 + Br\cdot$$
$$\text{(D)}$$

$$CCl_3CH_2CH=CH_2 \xrightarrow{\;CCl_4\;} CCl_3CH_2CHCH_2CCl_3 \xrightarrow{\;BrCCl_3\;}$$
$$\qquad\qquad\qquad\qquad\qquad \cdot CCl_3 + CCl_3CH_2CHBrCH_2CCl_3 \qquad (21)$$
$$\text{(E)}$$

$$CH_2=CHCH_2Br + Br\cdot \longrightarrow CH_2Br\dot{C}HCH_2Br \xrightarrow{\;BrCCl_3\;}$$
$$\qquad\qquad\qquad\qquad\qquad \cdot CCl_3 + CH_2BrCHBrCH_2Br$$
$$\text{(F)}$$
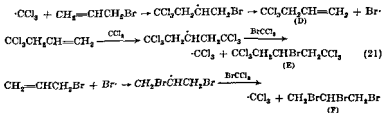
[18] W. S. Friedlander, *Am. Chem Soc Meeting Abstr*, 133, 18N (1958).
[19] Huyser and Echegaray, *J. Org Chem*, 27, 429 (1962).
[20] Kharasch and Sage, *J. Org. Chem*, 14, 537 (1949).

## Stereochemistry of Radical Additions

Radical additions to suitably substituted olefins can yield different possible stereoisomeric products: from open-chain olefins, *erythro* and *threo* pairs.   In general, both pairs are obtained, and it is noteworthy that in all carbon-radical additions which have been investigated the same mixture is obtained starting from the *cis-* or the *trans*-olefin.   The presumed explanation is that the intermediate radical undergoes free rotation about the former double bond at a rate which is rapid compared with reaction with the addend, AB.
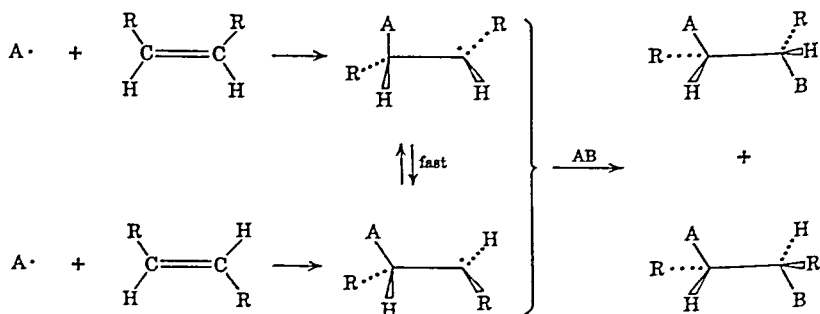


The stereochemistry of carbon radical additions to cyclic olefins has not been studied.   However, the addition of hydrogen bromide and of mercaptans is preferably *trans*,* and a similar result might be expected with carbon radicals.   Additions to the bridged norbornene system in contrast appear to give solely the *cis-exo* product, presumably for steric reasons, e.g., with ethyl bromoacetate.[21]



$$CH_2BrCO_2C_2H_5 \quad + \qquad\qquad\qquad \longrightarrow \qquad\qquad\qquad\qquad \tag{22}$$
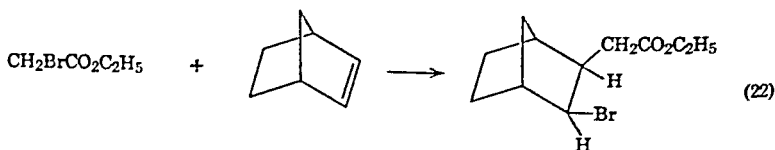
In additions to 1,3-dienes, attack of the resulting allylic radical on the addend can give rise to three possible products shown in (23).   In general, 1,4 addition is preferred, but the relative amounts of *cis* and *trans* product have not been investigated in detail.   From analogy to results in butadiene

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* See Chapter 4, pp. 157 and 173.
[21] J. Weinstock, *Am. Chem. Soc. Meeting Abstr.,* **128,** 19-O (1955).

$$A \cdot + CH_2=CH-CH=CH_2 \rightarrow \begin{matrix} ACH_2CH-CH=CH_2^* \\ \updownarrow \\ ACH_2CH-CH=CH_2 \end{matrix} \xrightarrow{AB}$$

$$\begin{matrix} ACH_2 & CH_2B \\ \diagdown & \diagup \\ C=C \\ \diagup & \diagdown \\ H & H \end{matrix} \quad + \quad \begin{matrix} ACH_2 & H \\ \diagdown & \diagup \\ C=C \\ \diagup & \diagdown \\ H & CH_2B \end{matrix} \quad + \quad ACH_2CHBCH=CH_2 \quad (23)$$
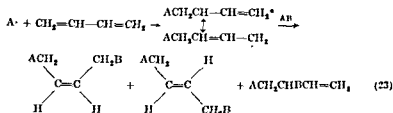
polymerization[22] and investigations of the stereochemistry of allylic radicals,[23] it might be expected that the *trans* product would predominate and its relative yield would be increased at lower temperatures.

## SCOPE AND LIMITATIONS

### Polyhalomethanes (Tables V–VIII)

As a class, the polyhalomethanes have received the greatest amount of study in radical addition reactions. Most of the successful additions have involved a tri- or tetra-halomethane, and displacement occurs on halogen in the order $I > Br > Cl$. Thus with bromotrichloromethane the reaction follows the course

$$CCl_3Br + CH_2=CHR \rightarrow CCl_3CH_2CHBrR$$

by way of the sequence

$$\cdot CCl_3 + CH_2=CHR \rightarrow CCl_3CH_2\dot{C}HR$$

$$CCl_3CH_2\dot{C}HR + CCl_3Br \rightarrow CCl_3CH_2CHBrR + \cdot CCl_3$$
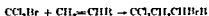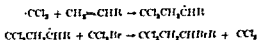
Reactions involving carbon tetrachloride and bromotrichloromethane are listed in Tables V and VI, respectively.

Iodotrifluoromethane is the only trifluoromethane that gives good yields of addition product (Table VII).

$$CF_3I + CH_2=CHR \rightarrow CF_3CH_2CHIR$$

of higher molecular weight may be built up by a stepwise process (rather than telomerization).[24]   While a four-center essentially non-radical reaction was suggested, it seems more likely that the products result from radical addition of initial 1:1 adducts to additional olefin.

Other polyhalomethane additions are listed in Table VIII. It is noteworthy that, in contrast to other polyhalomethanes, chloroform adds by hydrogen transfer; for example,

$$CHCl_3 + CH_2{=}CHR \rightarrow CCl_3CH_2CH_2R$$

via

$$\cdot CCl_3 + CH_2{=}CHR \rightarrow CCl_3CH_2\dot{C}HR$$
$$CCl_3CH_2\dot{C}HR + CHCl_3 \rightarrow CCl_3CH_2CH_2R + \cdot CCl_3$$
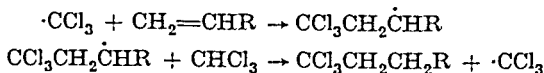
With polyhalomethanes less reactive than bromotrichloromethane, telomer formation is a serious complication in additions to simple olefins, although it can be minimized by working at high addend:olefin ratios. The other serious side reaction in halomethane additions is abstraction of allylic hydrogen, as discussed in the previous section.

### Aldehydes (Table IX)

The addition of an aldehyde to an olefin results in the formation of a ketone.

$$C_3H_7CHO + CH_2{=}CHR \rightarrow C_3H_7COCH_2CH_2R$$
$$C_3H_7\dot{C}O + CH_2{=}CHR \rightarrow C_3H_7COCH_2\dot{C}HR$$
$$C_3H_7COCH_2\dot{C}HR + C_3H_7CHO \rightarrow C_3H_7COCH_2CH_2R + C_3H_7\dot{C}O$$
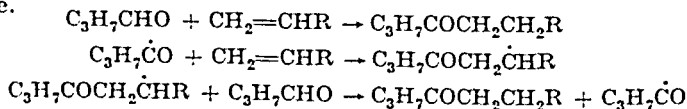
In some cases, the yields of 1:1 adducts are fairly good.   With simple olefins such as ethylene, telomer formation does occur.   Polar effects are important, and higher yields may be expected from additions of a given aldehyde to an olefin that has electron acceptor properties.   Perfluoro-olefins and olefins having carbonyl groups conjugated with the double bond fall in this category.

A side reaction which tends to lower the yields of ketones is the decarbonylation of the acyl radical.

## Alcohols (Table X)

Primary and secondary alcohols add to olefins to form secondary and tertiary alcohols, respectively

$$CH_3CH_2OH + CH_2=CHR \rightarrow CH_3CHOHCH_2CH_2R$$

via

$$CH_3\dot{C}HOH + CH_2=CHR \rightarrow CH_3CHOHCH_2\dot{C}HR$$

$$CH_3CHOHCH_2\dot{C}HR + CH_3CH_2OH \rightarrow CH_3CHOHCH_2CH_2R + CH_3\dot{C}HOH$$

Similarly,

$$(CH_3)_2CHOH + CH_2=CHR \rightarrow (CH_3)_2C(OH)CH_2CH_2R$$
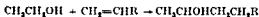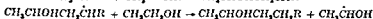
The addition of methyl alcohol to olefins results in the formation of primary alcohols

$$CH_3OH + CH_2=CHR \rightarrow HOCH_2CH_2CH_2R$$
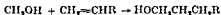
Tertiary alcohols, having no α-hydrogen atoms, do not add to olefins in a free radical chain reaction.

In all reported additions of alcohols to alkenes telomers are formed. With perfluoroölefins, fairly high yields of 1:1 addition products can be obtained, presumably because of favorable polar contributions in the chain transfer reaction. The tendency toward telomer formation with a given olefin is $CH_3OH > $ primary alcohol $>$ secondary alcohol. With high alcohol to olefin ratios and a sufficiently high reaction temperature, fairly good yields of 1:1 adducts can be obtained with secondary alcohols.

Although some photoinitiated additions of alcohols to olefins have been reported, the most notable success has been obtained with reactions initiated by di-t-butyl peroxide. Acyl peroxides undergo an induced decomposition with alcohols and are generally not effective initiators. (See the discussion of initiators, pp. 112–117) However, benzoyl peroxide has been used successfully to initiate additions of alcohols to perfluoroalkenes. Azobis(isobutyronitrile) is also ineffective as an initiator for alcohol additions, presumably because of the stability of the initiator radical

## Amines (Table XI)

In contrast to most polar reactions of amines, their radical addition to olefins involves the hydrogen atom on a carbon atom bonded to nitrogen. For example, piperidine adds to 1-octene to form 2-octylpiperidine



$$n\text{-}C_6H_{13}CH=CH_2 + \ \underset{H}{\overset{H}{N}} \rightarrow \underset{H}{\overset{H}{N}} CH_2CH_2C_6H_{13} \ n$$
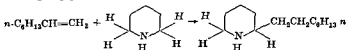
The chain sequence for this addition is
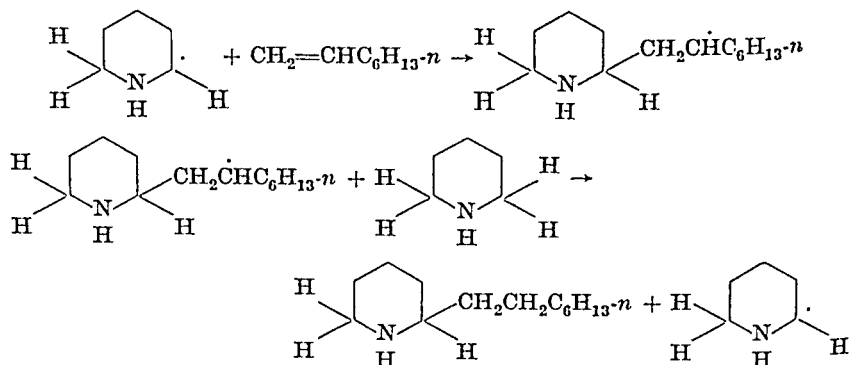


Additions of amines are generally initiated with di-$t$-butyl peroxide. Although some of these additions have been initiated photochemically, the reactions of amines with acyl peroxides render these peroxides ineffective as initiators. (See the discussion of initiators, pp. 112–117).

## Formic Acid Derivatives (Table XII)

Methyl formate is the only formate ester which has led to isolable products in free radical addition reactions. In the addition of methyl formate to $n$-alkenes the carbonyl-bonded hydrogen atom, as in aldehydes, undergoes abstraction in the transfer step yielding methyl esters as addition products.

$$HCO_2CH_3 + n\text{-}C_6H_{13}CH{=}CH_2 \rightarrow n\text{-}C_6H_{13}CH_2CH_2CO_2CH_3$$

via

$$\cdot CO_2CH_3 + n\text{-}C_6H_{13}CH{=}CH_2 \rightarrow n\text{-}C_6H_{13}\overset{\cdot}{C}HCH_2CO_2CH_3$$

$$n\text{-}C_6H_{13}\overset{\cdot}{C}HCH_2CO_2CH_3 + HCO_2CH_3 \rightarrow$$

$$n\text{-}C_6H_{13}CH_2CH_2CO_2CH_3 + \cdot CO_2CH_3$$
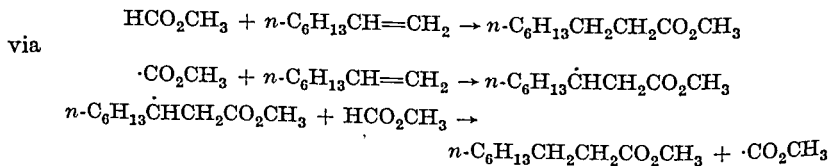
In all reported additions of methyl formate, a considerable amount of telomeric product was formed and yields of 1:1 addition product were somewhat modest at best.

Ethyl formate, although it participates in a chain reaction with ethylene, leads to a mixture of products. Not only the carbonyl-bonded hydrogen atom undergoes abstraction in the transfer step yielding ethyl esters as addition products, but the abstraction of a hydrogen atom from the alcohol portion of the ester also occurs yielding formic esters of telomeric secondary alcohols.

N-Alkyl formamides react to form a mixture of products. Abstraction of the carbonyl-bonded hydrogen atom in the transfer step results in the

formation of the N-alkyl amides of carboxylic acids. However, the transfer process can also involve the hydrogen atoms of the nitrogen-bonded alkyl portion of the molecule yielding telomeric N-alkyl formamides as products

The additions were initiated with di-t-butyl peroxide, benzoyl peroxide having proved ineffective Attempts at photochemical initiation in the case of methyl formate were also unsuccessful, considerable amounts of carbon monoxide and methanol were formed.

## Esters and Acids (Table XIII)

A hydrogen atom of a methylene group such as that in malonic ester, acetoacetic ester, or methyl cyanoacetate is readily abstracted by free radicals The resulting free radical readily adds to terminal olefins A free radical chain sequence involving these reactions yields the alkylated ester. For example, malonic ester and 1-octene react to form n-octyl-malonic ester.

$$CH_2(CO_2C_2H_5)_2 + n-C_6H_{13}CH=CH_2 \rightarrow n-C_8H_{17}CH_2CH(CO_2C_2H_5)_2$$

via

$$CH_2(CO_2C_2H_5)_2 + n-C_6H_{13}CH=CH_2 \rightarrow n-C_6H_{13}\dot{C}HCH_2CH(CO_2C_2H_5)_2$$

$$n-C_6H_{13}\dot{C}HCH_2CH(CO_2C_2H_5)_2 + CH_2(CO_2C_2H_5)_2 \rightarrow$$
$$n-C_6H_{13}CH_2CH_2CH(CO_2C_2H_5)_2 + \dot{C}H(CO_2C_2H_5)_2$$
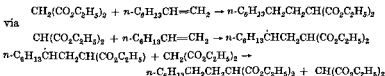
This method of alkylating active methylene compounds has been employed with success under proper experimental procedures (a high ratio of ester to olefin and a high reaction temperature), and 1.1 addition products have been obtained in good yield. Other esters and acids can also be alkylated in the α position in this manner.

Certain α-halo esters add to olefins in reactions involving the transfer of a halogen atom. For example, the addition of ethyl α-bromoacetate to 1-octene yields ethyl γ-bromocaprate.

$$BrCH_2CO_2C_2H_5 + n-C_6H_{13}CH=CH_2 \rightarrow n-C_6H_{13}CHBrCH_2CH_2CO_2C_2H_5$$

via

$$\cdot CH_2CO_2C_2H_5 + n-C_6H_{13}CH=CH_2 \rightarrow n-C_6H_{13}\dot{C}HCH_2CH_2CO_2C_2H_5$$

$$n-C_6H_{13}\dot{C}HCH_2CH_2CO_2C_2H_5 + BrCH_2CO_2C_2H_5 \rightarrow$$
$$n-C_6H_{13}CHBrCH_2CH_2CO_2C_2H_5 + \cdot CH_2CO_2C_2H_5$$
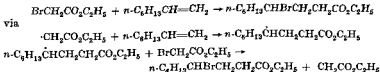
Other acid derivatives, e g , nitriles and acid chlorides, undergo comparable reactions and are included in Table XV.

Most ester addition reactions were initiated with di-t-butyl peroxide, although the reactions involving the halo esters were initiated with benzoyl peroxide and azobis(isobutyronitrile)

## Ethers and Acetals (Table XIV)

The work in this area of Kharasch additions is somewhat limited and the examples are taken largely from the patent literature. These additions involve the hydrogen atoms on a carbon atom bonded to oxygen in the transfer step, and subsequent addition of the ether radical to the olefin in the chain sequence as shown for the addition of methylal to maleic anhydride.
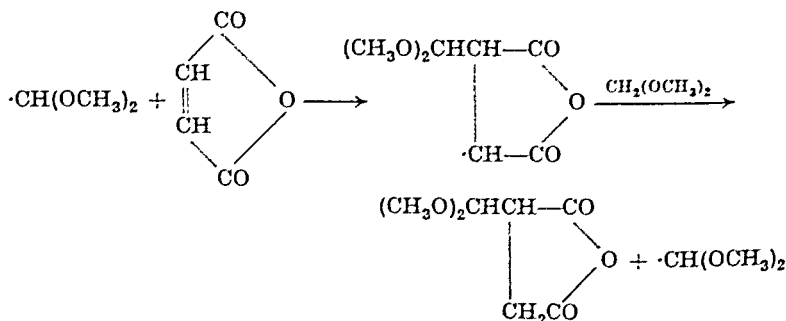


Most successful additions of ethers or acetals are to unsaturated compounds that will give favorable polar contributions both in the addition and in the chain transfer steps of the chain sequence. Maleic anhydride, $\alpha,\beta$-unsaturated esters, and perfluoroölefins have been used with success.

### Miscellaneous Additions

A few other types of molecules which undergo radical addition to olefins are collected in Table XV. It is worth noting that, at very high temperatures and pressures, radical additions of simple alkanes to olefins occur, initiated either thermally or by high-energy radiation. However, since such reactions lie outside the range of usual laboratory practice, they are not treated in detail.

#### INITIATION

The factors involved in the initiation of Kharasch addition reactions are extremely important in determining yields and in dictating the choice of reaction conditions. The methods of initiation, i.e., the introduction of free radicals in the reaction mixture, can be divided into three general types: (1) chemical initiation, (2) photoinitiation, and (3) high-energy radiation. Chemical initiators have the advantages of ease of handling and modest equipment requirements but have disadvantages in their temperature requirements and in the side reactions they may undergo.

Photoinitiation and high-energy radiation are temperature-independent and do not require the addition of chemical reagents to the reaction mixture. However, they require more elaborate equipment

## Chemical Initiators

Two chief types of initiators have been used to induce Kharasch addition reactions: organic peroxides and azobis(nitriles) The common feature of these materials is that, in the absence of any induced reactions, they can be
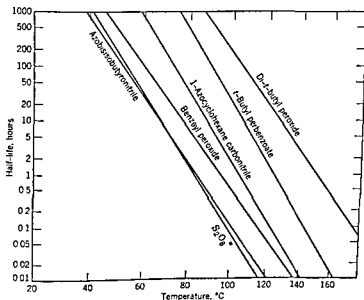


Fig 3. Half lives of some common initiators as a function of temperature. From C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc , New York, 1957, p 469

decomposed thermally into free radicals in a first-order reaction. Figure 3 shows the half-lives of some of the initiators useful in starting free radical chain reactions at ordinary temperatures (0–200°)

Since addition reactions require a continual supply of radicals to start chains, it is evident that with a given initiator a temperature should be chosen so that the desired reaction time corresponds to not more than a few half-lives of the initiator. Alternatively, the reaction may be carried out

at a higher temperature with continuous or incremental addition of the initiator.

The chemistry of these chemical initiators can best be discussed in terms of dialkyl peroxides, acyl peroxides, and azobis(nitriles).

**Dialkyl Peroxides.** The most readily available and widely used compound of this class is di-*t*-butyl peroxide (DTBP). This material undergoes the following smooth first-order decomposition both in solution and in the gas phase.

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$
$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot$$
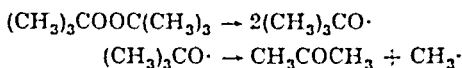
The extent of the secondary reaction is dependent on the reactivity of the solvent toward the *t*-butoxy radical formed in the primary reaction. The primary reaction, *which is rate-determining*, has a half-life of about 20 hours at 120°. The half-life decreases to about 1 hour at 150°, making this material a useful initiator in the temperature range 110–150°. This temperature range makes di-*t*-butyl peroxide useful in addition reactions involving an addend with a low chain transfer constant at lower temperatures. Indeed, the reason certain additions are feasible with di-*t*-butyl peroxide as the initiator may be that the temperature required to start the reaction is high enough to let the transfer reaction compete successfully with the polymerization step.

Advantages of di-*t*-butyl peroxide over acyl peroxides are that it shows little tendency to undergo induced decomposition and that its rate of decomposition is solvent independent. Furthermore, the radicals formed, *t*-butoxy radicals in the initial decomposition and methyl radicals in the possible elimination reaction, are both very reactive and capable of participating in steps which will start the desired free radical chain reaction.

Dicumyl peroxide, which is now commercially available, has received less study.

**Acyl Peroxides.** The most familiar examples of this class of peroxides are benzoyl peroxide and acetyl peroxide. These peroxides are thermally decomposed according to the scheme

$$
\begin{array}{ccc}
O & O & O \\
\| & \| & | \\
RCOOCR & \rightarrow & 2RCO\cdot \\
\end{array}
$$

$$
\begin{array}{c}
O \\
\| \\
RCO\cdot \rightarrow R\cdot + CO_2 \\
(R = CH_3 \text{ or } C_6H_5)
\end{array}
$$
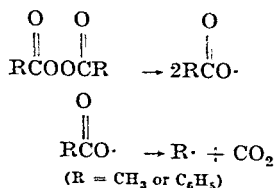
The decomposition of acetyl peroxide appears to proceed almost entirely to furnish methyl radicals and carbon dioxide. Benzoyl peroxide, on the

other hand, does give evidence of a benzoyloxy radical in its decomposition, and the amount of the secondary elimination reaction is dependent on the nature of the reagents with which the benzoyloxy radical may react.

The first-order decomposition rate of these peroxides is such that they have reasonable half-lives in the range 50–100°. However, the rate of disappearance of an acyl peroxide is also dependent on its environment, certain solvents being capable of causing a rapid induced decomposition which renders most of the peroxide ineffective as an initiator for the desired chain reaction.

The chemistry of the induced decomposition of benzoyl peroxide by ethers was investigated by Cass [25] The ether radical formed by abstraction of an α-hydrogen atom by a peroxide radical fragment reacts very rapidly with unreacted peroxide, yielding 1-ethoxyethyl benzoate and propagating a chain reaction as shown in the reaction of benzoyl peroxide with diethyl ether.

$$CH_3\overset{\cdot}{C}HOC_2H_5 + C_6H_5CO\overset{O}{\overset{\|}{O}}OC\overset{O}{\overset{\|}{C}}C_6H_5 \rightarrow CH_3\overset{H}{\underset{\underset{OC_2H_5}{|}}{\overset{O}{\overset{\|}{C}}}}OCC_6H_5 + C_6H_5C\overset{O}{\overset{\|}{O}}$$

$$C_6H_5C\overset{O}{\overset{\|}{O}} + CH_3CH_2OC_2H_5 \rightarrow C_6H_5C\overset{O}{\overset{\|}{O}}OH + CH_3\overset{\cdot}{C}HOC_2H_5$$
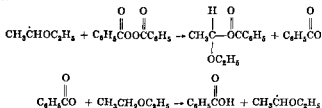
Primary and secondary alcohols induce the decomposition of acyl peroxides in a similar manner with resulting oxidation of the alcohol to an aldehyde or ketone [26] Acyl peroxides also react rapidly with amines, apparently chiefly by a non-radical path [27] Because of these reactions acyl peroxides are obviously poor choices for the initiation of chain additions of ethers, alcohols, and amines to olefins They have, however, been used successfully to initiate other additions; e g , the *lower-temperature* requirements of acyl peroxides render them useful in additions of aldehydes where the higher temperature required for dialkyl peroxides might lead to excessive decarbonylation.

**Azobis(nitriles).** The most familiar example of this type of initiator is azobis(isobutyronitrile) This compound undergoes a first-order decomposition in the manner shown. The decomposition rate is not affected by

$$(CH_3)_3C\overset{CN}{\underset{|}{-}}N{=}N{-}C(CH_3)_2\overset{CN}{\underset{|}{-}} \rightarrow 2(CH_3)_2\overset{CN}{\underset{|}{C}} + N_2$$
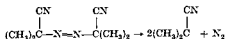
[25] Cass, *J. Am. Chem. Soc* , **69**, 500 (1947)
[26] Kharasch, Friedlander, and Urry, *J Org Chem* , **14**, 91 (1949)
[27] Walling and Indictor, *J Am. Chem Soc* , **80**, 5814 (1958)

the environment, the material decomposing at essentially the same rate in a variety of solvents. The half-life of azobis(isobutyronitrile) is about 20 hours at 60° making it useful as an initiator in the temperature range from 40° to 80°. By varying the substituents, azobis(nitriles) that decompose at other temperatures may be obtained.

Although azobis(isobutyronitrile) does not show induced decomposition the resulting *cyanoisopropyl* radical is quite unreactive, so its efficiency as an initiator is often quite low. Accordingly its use is restricted to highly reactive olefins or addends such as bromotrichloromethane.

**Other Chemical Initiators.** A variety of other compounds are known which undergo thermal decomposition into radicals and might be expected to induce radical addition processes, but they have not been investigated in detail. Peresters such as *t*-butyl perbenzoate decompose at rates intermediate between dialkyl and diacyl peroxides. Hydroperoxides also yield radicals, but at rates which appear to be highly solvent-dependent and which are also complicated by induced decomposition. A number of radical-producing redox systems are known, such as the combination of ferrous ion and hydroperoxide, which reacts as follows.

$$ROOH + Fe^{+2} \rightarrow RO\cdot + Fe^{+3} + {}^-OH$$
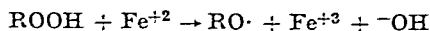
All of these can undoubtedly be used in suitable systems and it is worth noting that some olefin-addend systems often react spontaneously on heating, perhaps as the result of dissociation of adventitious peroxidic impurities.

## Photoinitiation

Ultraviolet light has been used successfully in many instances to initiate free radical addition reactions. On absorbing electromagnetic radiation a compound is excited to a higher electronic energy level. The amount of energy absorbed depends on the frequency of the radiation according to the relation

$$E = h\nu$$

where $h$ is Planck's constant and $\nu$ is the frequency of the vibration. In the ultraviolet range (4000–2000 Å), the energy absorbed amounts to 71.4–142.8 kcal/mole. This is sufficient to rupture covalent bonds in an organic compound. Most organic compounds absorb radiation in this range, but the absorption does not necessitate a dissociation into free radicals. Other non-radical reactions or phenomena associated with absorption such as fluorescence or loss of the absorbed energy in collision with other molecules, particularly in the liquid phase, can also serve as

outlets for the absorbed energy    In some cases, however, the molecule is dissociated directly on absorption of light into free radicals, and light serves as a useful means of initiation

The feasibility of using light to initiate the free radical reaction is dependent on the system involved    Some compounds absorb light in the near ultraviolet (3000 Å or above) and are dissociated very readily into free radicals    Bromotrichloromethane is one good example, and additions of this compound are readily initiated by illuminating reaction mixtures with ordinary sunlight or with a commercial sunlamp    Pyrex, however, is not transparent to light of shorter wavelength than 3000 Å    If the reactants require light below the lower limit of transparency of Pyrex, another container such as quartz, which is transparent to ultraviolet irradiation, is required    Production of ultraviolet light of lower wavelengths requires mercury vapor lamps or some other source of illumination

Photoinitiation has proved useful in several addition reactions of polyhalomethanes and certain alcohols and amines    The ultraviolet absorption characteristics of other compounds suggest the feasibility of photoinitiated addition reactions    However, the possibility of photochemical reactions other than the desired initiation process exists    For example, methyl formate when illuminated undergoes extensive decomposition into carbon monoxide and methyl alcohol with no detectable amount of addition product in the presence of 1-octene    Aldehydes and ketones illuminated in the presence of non-terminal olefins and acetylenes yield derivatives of trimethylene oxide [28]

$$R_2C{=}CR_2 + R_2C{=}O \xrightarrow{h\nu} \begin{array}{c} R_2C{-}CR_2 \\ | \quad\quad | \\ O{-}CR_2 \end{array}$$
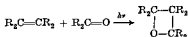
## High-Energy Radiation

The use of $\alpha$ and $\beta$ particles, $\gamma$ rays, and x-rays to initiate free radical chain reactions has received a considerable amount of attention in the last few years    The effect of such high-energy radiation on organic matter is complex and involves initially chiefly the stripping of electrons from molecules to form ions    However, in secondary processes a significant amount of the total energy absorbed (up to perhaps 20 %) may go into the homolytic cleavage of bonds to form radicals    These radicals in turn can induce radical addition processes, but the often low radical yields and the complex equipment and shielding required make the technique rather marginal for synthetic purposes except under rather special conditions.

[28] Buchi, Inman, and Lipinsky, J. Am. Chem Soc , 76, 4327 (1954)

## EXPERIMENTAL CONDITIONS

### Purity of Reagents

Since the reactions with which we are dealing are chain processes, traces of impurities which can interrupt chains can greatly lower yields or prolong reaction times. Accordingly, it is generally desirable to work with freshly distilled reagents of known purity. Reactive monomers such as vinyl acetate and styrene must be freed of inhibitors that have been added to prevent polymerization during storage. Phenolic inhibitors can be removed by extraction with dilute aqueous base before distillation. In some cases, trace impurities which cannot be readily removed can effectively be "burned up" by the use of additional initiator. Since oxygen commonly interferes with radical chain processes, yields may be improved and reactions accelerated by the use of an inert atmosphere or by vigorous boiling to displace air from the system. Metal salts may also interfere in some systems, and when reactions fail in metal vessels contamination should be suspected.

### Concentration of Reactants

The most serious side reaction encountered in attempting to prepare simple 1:1 addition products is the formation of telomers. Telomers result from addition of the adduct radical to another molecule of olefin instead of chain transfer with a molecule of adding reagent. The rate of the addition reaction can obviously be minimized by lowering the concentration of the olefin. Consequently, in systems where the chain transfer constant is less than one, it is preferable to use a high molar ratio of adding reagent to olefin. One method of accomplishing this is to add the olefin to the reaction mixture very slowly, allowing the previously added portion to undergo almost complete reaction before more olefin is added. This procedure has made possible the formation of 1:1 addition products in good yields even with highly polymerizable monomers such as vinyl acetate. Where experimental conditions prohibit such slow addition, it is advisable to begin with a high concentration of the adding reagent with respect to the olefin.

### Temperature

When telomer formation is a serious complication, it can often be diminished by increasing the reaction temperature. Thus many addition reactions which give low yields of 1:1 addition products at 50–80°, a temperature range suitable for such initiators as benzoyl peroxide, acetyl

peroxide, and azobis(isobutyronitrile), might be expected to give higher yields if initiated with di-t-butyl peroxide, an initiator effective in the range 120–150°

Complications may, of course, arise in carrying out reactions with low-boiling reagents at elevated temperatures  In some cases, slow addition of the more volatile component is satisfactory, as in the reaction of vinyl acetate with dimethyl malonate  Otherwise, the use of pressure equipment is required

## EXPERIMENTAL PROCEDURES

*t-Amyl Alcohol (Addition of Isopropyl Alcohol to Ethylene).*[23] A solution of 4 5 g  (0 03 mole) of di-t-butyl peroxide in 425 g  (7 07 moles) of isopropyl alcohol is heated to 125–130° in a glass-lined stainless steel autoclave  A pressure of ethylene of 200–300 lb /sq in. is maintained above the solution and the gas is mixed with the liquid by means of a Magnedash stirrer  In 20 hours, approximately 2 0 moles of ethylene reacts. Distillation of the reaction mixture yields a low-boiling fraction consisting of the peroxide decomposition products, acetone and t-butyl alcohol  After removal of the unreacted isopropyl alcohol by distillation, the 1:1 addition product is collected at 66°/165 mm  The yield of t-amyl alcohol ($n_D^{20}$ 1 4052) is 76 g , 36% based on the ethylene reacted

Further fractionation of the reaction mixture gives 24 2 g  of the 2:1 addition product, 2 methyl-2-hexanol (82°/80 mm , $n_D^{20}$ 1 4180) ; 16 0 g. of the 3:1 addition product, 2-methyl-2-octanol (66°/8 mm , $n_D^{20}$ 1.4282); and 10 5 g. of the 4:1 addition product, 2-methyl-2-decanol (75°/0.3 mm., $n_D^{20}$ 1.4368)  A residue of 18 5 g  with an average molecular weight of 274 remains

**3,3-Dicarbomethoxypropyl Acetate (Addition of Dimethyl Malonate to Vinyl Acetate).**[30] In a 500-ml flask equipped with a condenser and a dropping funnel, 198 g  (1.5 moles) of dimethyl malonate is heated to 150–152°. A mixture of 12 9 g  (0.15 mole) of vinyl acetate and 4 4 g. (0 03 mole) of di-t-butyl peroxide is added from the dropping funnel to the heated ester during 4 hours. The reaction mixture is heated for an additional 30 minutes, then the peroxide decomposition products and unreacted dimethyl malonate are removed by vacuum distillation. Fractionation of the high-boiling residue yields 21 g. (65% based on vinyl acetate) of 3,3 dicarbomethoxypropyl acetate (108–115°/3 mm., $n_D^{20}$ 1.4370, mol. wt 216).  About 0.5 g  of tetramethyl ethane-1,1,2,2-tetra-carboxylate (m p  135°) and 19 0 g  of a telomeric residue having an average molecular weight of 488 are also obtained

[23] Urry, Stacey, Huyser, and Juveland, J Am Chem Soc , 76, 450 (1954)
[30] R Gritter, Ph D Thesis, University of Chicago, 1955

1-Iodoheptafluoropropane (Addition of Trifluoroiodomethane to Perfluoroethylene).[31]   A mixture of trifluoroiodomethane and perfluoroethylene in a 10:1 molar ratio is sealed in a Pyrex reaction tube.   The liquid phase of the mixture is exposed to ultraviolet radiation for 3 hours, after which the reaction mixture is recharged with the same quantity of olefin and the illumination repeated for 3 hours.   After removal of the unreacted trifluoroiodomethane, the 1:1 addition product, 1-iodoheptafluoropropane, is collected at 39–40°.   The yield is 94%, based on the olefin added.

Diethyl $n$-Butyrylsuccinate (Addition of $n$-Butyraldehyde to Diethyl Maleate).[32]   A mixture of 72.0 g. (1.0 mole) of $n$-butyraldehyde, 43.0 g. (0.25 mole) of diethyl maleate, and 2.0 g. (0.008 mole) of benzoyl peroxide is heated at the reflux temperature for 18 hours.   During the heating, the temperature rises from 82° to 88°.   The reaction mixture is cooled, extracted with aqueous sodium bicarbonate, washed twice with water, and dried over sodium sulfate.   Removal of the unreacted aldehyde by distillation gives the crude 1:1 addition product, diethyl $n$-butyrylsuccinate (47 g., 76%, b.p. 95–108°/0.5 mm.), and 12 g. of a higher-boiling, yellow, slightly viscous residue.   Redistillation of the crude diethyl $n$-butyrylsuccinate gives 32 g. of pure product; b.p. 112–114°/1 mm., $n_D^{25}$ 1.4349.

1,1,1-Trichloro-3-bromo-3-phenylpropanol (Addition of Bromotrichloromethane to Styrene).[33]   A solution of 100 g. of bromotrichloromethane, 12 g. of styrene, and 2.3 g. of acetyl peroxide is heated to 60–70° for 4 hours.   Distillation of the reaction mixture through a 10-in. Vigreux column gives 78 g. of unreacted bromotrichloromethane (b.p. 103–104°) and 27 g. of 1,1,1-trichloro-3-bromo-3-phenylpropane (b.p. 92°/0.2 mm.).   The adduct quickly solidifies to a white crystalline mass and, after one recrystallization from methanol, melts at 54.5–55.0°.   After removal of the 1:1 addition product, 6 g. of a high-boiling residue remains.

1,1,1,3-Tetrachlorononane (Addition of Carbon Tetrachloride to 1-Octene).[34]   Carbon tetrachloride (154 g., 1.0 mole), 1-octene (37 g., 0.33 mole), and benzoyl peroxide (5 g., 0.02 mole) are heated under reflux for 4 hours under a positive pressure of nitrogen (15 cm. of mercury).   During the heating, the temperature rises from 90° to 105°.   Removal of excess carbon tetrachloride by distillation leaves a residue which yields on vacuum distillation 72 g. of crude 1:1 addition product

[31] Haszeldine, *J. Chem. Soc.*, 1953, 3761.
[32] Patrick, *J. Org. Chem.*, 17, 1009 (1952).
[33] Kharasch, Reinmuth, and Urry, *J. Am. Chem. Soc.*, 69, 1105 (1947).
[34] Kharasch, Jensen, and Urry, *J. Am. Chem. Soc.*, 69, 1100 (1947).

(b p 75–85°/0 05 mm ) and 13 g of higher telomers    Redistillation of the crude product gives 66 g  (75 %) of 1,1,1,3-tetrachlorononane,  b p 78–79°/0 1 mm , $n_D^{25}$ 1 4770

## TABULAR SURVEY
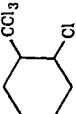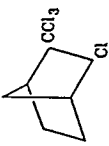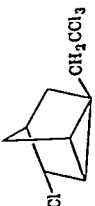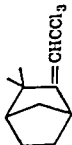
The following tables list various addition reactions according to the type of addend    They include reactions that could be found in a literature survey up to April 1962   *Chemical Abstracts* were covered in this survey up to January 1962   The reactions chosen for this tabulation are those which yielded simple addition products with the indicated unsaturated species    In some cases a reaction which led to telomeric products was included to illustrate that addition does occur to the unsaturated compound listed.

In tables containing several addends, the addends are listed in order of increasing number of carbon atoms    The unsaturated compounds are listed in the following order   alkenes and alkynes in order of increasing number of carbon atoms, halogenated alkenes, unsaturated compounds with oxygen-containing functions, and, finally, unsaturated compounds with other atoms    The method of initiation of the reactions is indicated, where possible, by the following symbols:  $Bz_2O_2$, benzoyl peroxide;  $Ac_2O_2$, acetyl peroxide;  DTBP, di-$t$-butyl peroxide;  AIBN, azobis-(isobutyronitrile);  $h\nu$, photoinitiation;  Thermal, thermal initiation;  $\gamma$, initiation by gamma rays;  and Per., peroxidic agents, generally benzoyl or acetyl peroxide.

The yield of addition product listed is the highest reported under the experimental conditions in the indicated reference.  The experimental conditions are not listed in these tables (however, see the following paragraph), since it is the authors' belief that in many cases they are not the optimum conditions    Proper modifications of the experimental procedure, such as varying the ratio of addend to unsaturated compound or raising the temperature, might in many cases result in considerable increase in the yield of the 1:1 addition product.  The yields reported in the tables do, however, indicate to some degree the potential synthetic usefulness of the reaction.

Some information about reaction temperatures can be obtained from the initiator used   Reactions initiated with benzoyl peroxide were generally carried out at 60–90°.  The same temperature range is generally employed for reactions initiated by acetyl peroxide and azobis(isobutyronitrile), although in some instances slightly lower temperature ($<50°$) are possible.  Reactions induced with di $t$-butyl peroxide were carried out at 110–160°, a temperature range in which the peroxide yields free radicals at a rate useful for starting chains.
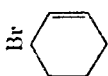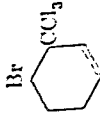
## TABLE V

### ADDITION OF CARBON TETRACHLORIDE

| Olefin | Initiator | 1:1 Addition Product(s) | Yield of 1:1 Adduct, % (Telomers) | Refs. |
|---|---|---|---|---|
| Ethylene | $Bz_2O_2$ | $Cl_3CCH_2CH_2Cl$ | plus telomers | 34–37 |
| Propylene | $Bz_2O_2$ | $Cl_3CCH_2CHClCH_3$ | 90 | 38 |
| Isobutylene | $Bz_2O_2$ | $Cl_3CCH_2CCl(CH_3)_2$ | 78 | 39, 40 |
| 1,3-Butadiene | $Bz_2O_2$ | $Cl_3CCH_2CH=CHCH_2Cl$ | 23 | 41 |
| t-Butylethylene | $Bz_2O_2$ | $Cl_3CCH_2CHClC(CH_3)_3$ | — | 42 |
| Biallyl | — | $Cl_3CCH_2CHCl(CH_2)_2CH=CH_2$ | 26 | 34 |
| | | $Cl_3CCH_2CHCl(CH_2)_2CHClCH_2CCl_3$ | 31 | |
| Cyclohexene | $Bz_2O_2$ |  | — | 42, 43 |
| 1-Heptene | $Bz_2O_2$ | $Cl_3CCH_2CHClC_5H_{11}\text{-}n$ | 72 | 42, 44 |
| Norbornene | $Bz_2O_2$ |  | 56 | 45 |
| 1-Octene | $Ac_2O_2$ | $Cl_3CCH_2CHClC_6H_{13}\text{-}n$ | 85 | 34, 46 |
| 5-Methylenebicyclo[2.2.1]hept-2-ene | $Bz_2O_2$ |  | — | 19 |
| Camphene | $Ac_2O_2$ |  | — | 47, 48 |

| Monomer | Catalyst | Product | Yield (%) | References |
|---|---|---|---|---|
| Limonene | $Bz_2O_2$ | (structure) | 70 | 49, 50 |
| β-Pinene | $Bz_2O_2$ | (structure) | 97 | 50–52 |
| Allylbenzene | $Ac_2O_2$ | $Cl_3CCH_2CHClCH_2C_6H_5$ | 25 | 53 |
| o-Methoxyallylbenzene | $Ac_2O_2$ | $Cl_3CCH_2CHClC_6H_4OCH_3\text{-}o$ | 50 | 53 |
| p-Methoxyallylbenzene | $Ac_2O_2$ | $Cl_3CCH_2CHClC_6H_4OCH_3\text{-}p$ | 23 | 53 |
| m-Methylallylbenzene | $Ac_2O_2$ | $Cl_3CCH_2CHClC_6H_4CH_3\text{-}m$ | 24 | 53 |
| p-Methylallylbenzene | $Ac_2O_2$ | $Cl_3CCH_2CHClC_6H_4CH_3\text{-}p$ | 29 | 53 |
| 1-Hexadecene | $Ac_2O_2$ | — | — | 42 |
| Vinyl acetate | $Bz_2O_2$ | $Cl_3CCH_2CHClOOCCH_3$ | (Telomers) | 39 |
| Allyl chloride | $Bz_2O_2$ | $Cl_3CCH_2CHClCH_2Cl$ | (Telomers) | 54, 55 |
| Allyl acetate | $Bz_2O_2$ | $Cl_3CCH_2CHClCH_2OOCCH_3$ | (Telomers) | 33, 39 |
| Vinyl ethyl ether | $Bz_2O_2$ | $Cl_3CCH_2CHClOC_2H_5$ | 65 | 56 |
| Vinyl n-butyl ether | AIBN, $h\nu$ | $Cl_3CCH_2CHClOC_4H_9\text{-}n$ | 85 | 56, 57 |
| Vinyl cyclohexyl ether | AIBN, $h\nu$ | $Cl_3CCH_2CHClOC_6H_{11}\text{-}cyclo$ | 90 | 57 |
| Vinyl phenyl ether | AIBN, $h\nu$ | $Cl_3CCH_2CHClOC_6H_5$ | 87 | 56, 57 |
| Divinyl ether | AIBN | $(Cl_3CCH_2CHCl)_2O$ | 60 | 58 |
| $CH_2{=}CHCH(OC_4H_9)_2$ | $h\nu$ | $(C_4H_9O)_2CHCH_2{\cdots}$ | | 59 |
| $(CClH{=}CH)_2Hg$ | $Ac_2O_2, Bz_2O_4$ | $Cl_3CCH_2CHCl{\cdots}$ | 46 | 59 |
| $(CClH{=}CH)_2Hg$ | $Bz_2O_4$ | $Cl_3CCH{=}CHCl$ | 38 | 60 |
| $CH_2{=}CHCl(OC_4H_9)_2$ | AIBN | $Cl_3CCH_2CHCl(OC_4H_9){\cdots}$ | 45 | 61 |
| Butadiene sulfone | $Bz_2O_2$ | (structure) $+ Cl_3CCH_2CH{=}CHCH_2Cl$ | 62 | 47, 62 |
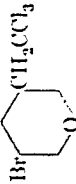
## TABLE VI
### ADDITION OF BROMOTRICHLOROMETHANE

| Unsaturated Compound | Initiation | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|
| Ethylene | $Ac_2O_2$ | $Cl_3CCH_2CH_2Br$ | — | 33, 63 |
| Propylene | $hv$ | $Cl_3CCH_2CHBrCH_3$ | — | 33 |
| 1-Butene | — | $Cl_3CCH_2CHBrC_2H_5$ | 43 | 63 |
| 2-Butene | $hv$ | $CH_3CH(CCl_3)CHBrCH_3$ | 13 | 64 |
| Isobutylene | $Ac_2O_2$ | $Cl_3CCH_2CBr(CH_3)_2$ | — | 33 |
| 1,3-Butadiene | — | $Cl_3CCH_2CH{=}CHCH_2Br$ | 75 | 65, 66 |
| 2-Methyl-2-butene | $hv$ | $Cl_3CCH(CH_3)CBr(CH_3)_2$ | 77 | 65 |
| Cyclopentene | — | (cyclopentane ring bearing $CCl_3$ and $Br$) | — | 67 |
| Cyclopentadiene | — | (cyclopentene ring bearing $Cl_3C$ and $Br$) | — | 67 |
| 2-Methyl-1-butene | $hv$ | $Cl_3CCH_2CBr(C_2H_5)_2$ | 91 | 65 |
| Cyclohexene | $hv$ | (cyclohexane ring bearing $Br$ and $CCl_3$) | 30 | 65, 67, 68 |
| 1,3-Cyclohexadiene | — | (cyclohexene ring bearing $Br$ and $CCl_3$) | 68 | 67 |
|  |  | (cyclohexadiene ring bearing $CCl_3$) | 32 |  |

| Compound | Catalyst | Product | Yield | Reference |
|---|---|---|---|---|
| Norbornene | — | (CCl₃/Br bicyclic structure) | — | 67 |
| 1-Octene | $hv$, $Ac_2O_2$ | $Cl_3CCH_2CHBrC_4H_{13}$-$n$ | 88 | 33, 65 |
| 2-Octene | $Ac_2O_2$ | $C_4H_9Cl_2Br$ | 45 | 69 |
| 1-Octyne | $Ac_2O_2$ | $Cl_3CCH=CHC_7H_{13}$-$n$ | 80 | 69 |
| 2-Octyne | $Ac_2O_2$ | $C_7H_{14}Cl_2Br$ | 33 | 69 |
| Bicyclo[2.2.1]oct 2-ene | — | (CCl₃/Br bicyclic structure) | — | 67 |
| Styrene | $Ac_2O_2$ | $Cl_3CCH_2CHBrC_6H_5$ | 78 | 33, 65, 66 |
| Phenylacetylene | $hv$ | $Cl_3CCH=CBrC_6H_5$ | 32 | 70 |
| α-Methylstyrene | $hv$ | $Cl_3CCH-CClCH_3C_6H_5$ | 40 | 66 |
| β-Methylstyrene | $hv$ | $Cl_3CCH(CH_3)CHBrC_6H_5$ | — | 65 |
| Allylbenzene | $hv$ | $Cl_3CCH_2CHBrCH_2C_6H_5$ | 44 | 65 |
| Indene | — | (CCl₃/Br indane structure) | — | 67 |
| Dicyclopentadiene | — | $C_{10}H_{14}Cl_3Br$ | — | 67 |
| $CF_2=CFCl$ | — | $CF_2ClCFClCF_2Br$ | — | 67 |
| $CF_2=CHCF_3$ | $hv$ | $CF_3CHFCF_2Br$ | — | 71 |
| Allyl alcohol | $Ac_2O_2$ | $Cl_3CCH_2CHClCH_2Cl$ | — | 72 |
| $CH_2=CClCH_3$ | $Bz_2O_2$ | $Cl_3CCH_2CClBrCH_3$ | 34 | 73 |
| $CH_2=CClCH_2Cl$ | $Bz_2O_2$ | $Cl_3CCH_2CClBrCH_2Cl$ | 8 | 33, 65 |
| $CHCl=CHCl_2$ | $Bz_2O_2$ | $Cl_3CCHClCHClCCl_3$ | 65 | 74 |

*Note.* References 35 to 160 are on pp. 147–149.

TABLE VI—*Continued*

ADDITION OF BROMOTRICHLOROMETHANE

| Unsaturated Compound | Initiation | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|
| Allyl bromide | $hv$ | $Cl_3CCH_2CHBrCH_2CCl_3$ | 37 | 70 |
| | | $Cl_3CCH_2CH=CH_2$ | — | |
| | | $BrCH_2CHBrCH_2Br$ | 41 | |
| $CH_2=CBrCH_3$ | $Bz_2O_2$ | $Cl_3CCH_2CBr_2CH_3$ | 50 | 74 |
| $CH_2=CBrCH_2Cl$ | $Bz_2O_2$ | $Cl_3CCH_2CBr_2CH_2Cl$ | 8 | 74 |
| $CH_2=C(CF_3)CH_3$ | $Bz_2O_2$ | $Cl_3CCH_2CBr(CF_3)CH_3$ | 64 | 74 |
| $CH_3CH=CClCH_3$ | $Bz_2O_2$ | $Cl_3CCH(CH_3)CClBrCH_3$ | 76 | 74 |
| $CH_2=C(CH_3)CH_2Cl$ | $hv$ | $Cl_3CCH_2CBr(CH_3)CH_2Cl$ | 45 | 74 |
| $CH_2ClCH=CHCH_2Cl$ | $Bz_2O_2$ | $CH_2ClCH(CCl_3)CHBrCH_2Cl$ | 23 | 74 |
| $CH_2ClCH=CClCH_3$ | $Bz_2O_2$ | $CH_2ClCH(CCl_3)CClBrCH_3$ | 8 | 74 |
| $CH_2=CHCH_2CCl_3$ | $hv$ | $Cl_3CCH_2CHBrCH_2CCl_3$ | — | 65 |
| p-Chlorostyrene | $hv$ | $Cl_3CCH_2CHBrC_6H_4(Cl-p)$ | 74 | 66 |
| 2,4-Dichlorostyrene | $hv$ | $Cl_3CCH_2CHBrC_6H_3Cl_2$-2,4 | 20 | 65 |
| Allyl ethyl ether | $Bz_2O_2$ | $Cl_3CCH_2CHBrCH_2OC_2H_5$ | 29 | 75 |
| Diallyl ether | — | ![structure] Br—[ring]—CH$_2$CCl$_3$ with O | — | 76 |
| Allyl β-chloro-α,β-trifluoroethyl ether | $Bz_2O_2$ | $Cl_3CCH_2CHBrCH_2OCF_2CHFCl$ | 50 | 75 |
| Vinyl acetate | $Ac_2O_2$ or $hv$ | $Cl_3CCH_2CHBrOCOCH_3$ | 90 | 33, 63, 65, 77, 78 |

| | | | | |
|---|---|---|---|---|
| Isopropenyl acetate | Bz₂O₂ or hv | Cl₃CCH₂CH(CH₃)OCOCH₃ | 27 | 66 |
| CH₂=CH(CH₃)₂CO·C₂H₅ | AIBN | Cl₃CCH—CH₂Cl₂CCOCH₃ | | 79 |
| CH₂CH=CHCO₂C₂H₅ | hv | Cl₃CCH₂CHBrCH₂CO₂C₄H₅ | 92 | 65 |
| Dimethyl furnarate | Bz₂O₂ | CH₃CH(CO₂CH₃)CHBrCO₂C₄H₅ | 84 | 80 |
| | hv | Cl₃CCOCH₃CH₃ | | 81, 82 |
| Dimethyl maleate | hv | BrCHCO₂CH₃ | | 81 |
| | | Cl₃CCHCO₂C₄H₅ | | |
| | | BrCHCO₂CH₃ | | |
| Ethyl cinnamate | Ac₂O₂ or Bz₂O₂ | Cl₃CCH(CO₂C₄H₅)CHBrC₄H₅ | 72 | 65, 80 |
| Allyl cyanide | Bz₂O₂ | Cl₃CCH₂CHBrCH₂CN | 65 | 65 |
| cis-Cinnamonitrile | Bz₂O₂ | Cl₃CCH(CN)CHBrC₄H₅ | | 80 |
| trans-Cinnamonitrile | Bz₂O₂ | Cl₃CCH(CN)CHBrC₄H₅ | 33 | 80 |
| Butadiene sulfone | Ac₂O₂ | Br[  ]CCl₃ SO₂ | 62 | 62 |
| CH₂=CHSiCl₃ | Bz₂O₂ | Cl₃CCH₂CHBrSiCl₃ | | 83 |
| CH₂=CHSi(Cl)₂CH₃ | hv | Cl₃CCH₂CHBrSi(Cl)₂CH₃ | | 83 |
| CH₂=CHSi(C₂H₅)₃ | Bz₂O₂ | Cl₃CCH₂CHBrSi(C₂H₅)₃ | 94 | 84 |
| CH₂=CHB(OC₄H₉ⁿ)₂ | AIBN | Cl₃CCH₂CHBrB(OC₄H₉ⁿ)₂ | 94 | 61 |
| CH₂=C(CH₃)BrO(C₄H₉ⁿ)₂ | AIBN | Cl₃CCH(CH₃)BrB·O(C₄H₉ⁿ)₂ | 90 | 85 |
| CH₂=CHCH=CHBrB·O(C₄H₉ⁿ)₂ | AIBN | | | 85 |
| CH₂CH₂HSn(C₄H₉)₃ | Bz₂O₃ | Cl₃CCH₂CH₂Sn(C₄H₉)₃ | 94 | 84 |

Note

## TABLE VII

### ADDITION OF IODOTRIFLUOROMETHANE

| Unsaturated Compound | Initiator | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|
| $CH_2{=}CH_2$ | hν or thermal | $CF_3CH_2CH_2I$ | 82 | 86 |
| $CH{\equiv}CH$ | hν | $CF_3CH{=}CHI$ | 78 | 87, 88 |
| $CH_2{=}CHF$ | hν | $CF_3CH_2CHFI$ | 65 | 89 |
| $CH_2{=}CHCl$ | hν | $CF_3CH_2CHClI$ | 47 | 89 |
| $CH_2{=}CF_2$ | hν | $CF_3CH_2CF_2I$ | 80 | 24 |
| $CF_2{=}CHCl$ | hν | $CF_3CF_2CHClI$ | — | 90 |
| $CHF{=}CF_2$ | — | $CF_3CHFCF_2I$ | 80 | 90 |
|  |  | $CF_3CF_2CHFI$ | 20 | 91 |
| $CF_2{=}CFCl$ | hν | $CF_3CF_2CFClI$ | Telomers | 92, 93 |
| $CF_2{=}CF_2$ | hν | $CF_3CF_2CF_2I$ | 94 | 86, 94, 95 |
| $CH_2{=}CHCH_3$ | hν or thermal | $CF_3CH_2CHICH_3$ | 50 | 86 |
| $CH_2{=}CHCF_3$ | hν | $CF_3CH_2CHICF_3$ | 68 | 72, 96 |
| $CF_2{=}CHCH_3$ | hν | $CF_3CH(CH_3)CF_2I$ | 77 | 97 |
| $CF_2{=}CHCF_3$ | hν | $(CF_3)_2CHCF_2I$ | 80 | 98 |
| $CF_2{=}CFCF_3$ | hν | $CF_3CF_2CFICF_3$ | Telomers | 99, 100 |
| $CH_2{=}CClCF_3$ | hν | $CF_3CH{=}CClCH_3$ | 91 | 101, 102 |
| $CH{\equiv}CCF_3$ | hν | $CF_3CH{=}CICF_3$ | — | 102 |
| $CH_2{=}C(CF_3)_2$ | hν | $CF_3CH_2CI(CF_3)_2$ | 71 | 97 |
| $CH_2{=}C(CF_3)CF_2Cl$ | hν | $CF_3CH_2CI(CF_3)CF_2Cl$ | 69 | 97 |
| $CH{\equiv}CC_2H_5$ | hν | $CF_3CH{=}CIC_2H_5$ | — | 102 |
| $CH_2{=}CHCN$ | hν | $CF_3CH_2CHICN$ | 72 | 103 |
| $CH_2{=}CHCO_2CH_3$ | hν | $CF_3CH_2CHICO_2CH_3$ | 38 | 89 |

Note: References 35 to 160 are on pp. 147–149.

## TABLE VIII

### ADDITION OF OTHER POLYHALOALKANES

| Polyhaloalkane | Unsaturated Compound | Initiator | Product(s) | Yield, % | Refs |
|---|---|---|---|---|---|
| $CH_2Cl$ | $CH_2=CH_2$ | — | $CH_2ClCH_2I$ | Telomers | 35 |
| $CHCl_3$ | $CH_2=CH_2$ | — | $CCl_3CH_3$ | Telomers | 35, 37 |
| | $CH_2=CHCH_3$ | $Ba_2O_2$ | $CCl_3CH_2CHClCH_3$ | Telomers | 6 |
| | 1,3 Butadiene | $As_2O_2$ | $CCl_3CH_2CH=CH(CH_2)_2CH=CH_2$ | | 104 |
| | $(CH_2=CHCl)_2$ | $As_2O_2$ | $CCl_3CH_2CHIC_6H_{13}^{n}$ | 45 | 34 |
| $CHCl_2Br$ | $CH_2=CHCl$ | $Bz_2O_2$ | $CCl_3CH_2CHBrCH_3$ | 45 | 34 |
| | $CH_2=CHCl$ | — | $CHCl_2CH_2CHBrCH_3$ | 5 | 105 |
| | $CH_2=C(CH_3)_2$ | — | $CHCl_2CHBrCH_3$ | 22 | 105 |
| | $CH_2=CHCl$ | — | $CHCl_2CH_2CHBrCH_3$ | — | 105 |
| | $CH_2=CHC_6H_{13}^{n}$ | — | $CHCl_2CH_2CHBrC_6H_{13}^{n}$ | — | 105 |
| | $CH_2=CHCOOCH_3$ | $As_2O_2$ | $CHCl_2CH_2CHBrCOOCH_3$ | — | 24 |
| $CHBr_3$ | $CH_2=CHC_{10}H_{21}^{n}$ | $Bz_2O_2$ | $CHBr_2CH_2CHBrC_{10}H_{21}^{n}$ | — | 34 |
| $CH_4$ | $CH_2=CHC_4H_9$ | $As_2O_2$ | $CHBr_2CH_2CHBrC_4H_9$ | 31 | 106 |
| | $CH_2=CHCH_2OOCC_4H_5$ | $As_2O_2$ | $CH_3CH_2CH=CHCH_2OOCC_4H_5$ | 10 | 106 |
| | Limonene | $As_2O_2$ | (cyclohexene: ring with $CH_3$ / $\cdot OCH_2CH_2$ / $CH_3$) | 35 | 106 |
| $CCl_4$ | $CH_2=CHCF_3$ | $hv$ | $CCl_3CH_2CHICF_3$ | 57 | 107 |
| | $CH=CCF_3$ | $hv$ | $CCl_3CH=CClCF_3$ | 74 | 107 |

*Note:* References 35 to 160 are on pp. 147–149.

TABLE VIII—Continued

ADDITION OF OTHER POLYHALOALKANES

| Polyhaloalkane | Unsaturated Compound | Initiator | Product(s) | Yield, % Telomers | Refs. |
|---|---|---|---|---|---|
| $CF_2Br_2$ | $CH_2{=}CH_2$ | $Bz_2O_2$ | $CF_2BrCH_2CH_2Br$ | 34 | 108 |
| | $CH_2{=}CHF$ | $Bz_2O_2$ | $CF_2BrCH_2CHFBr$ | 28 | 109 |
| | $CH_2{=}CF_2$ | $Bz_2O_2$ | $CF_2BrCH_2CF_2Br$ | 9 | 109 |
| | $CHF{=}CF_2$ | $Bz_2O_2$ | $CF_2BrCHFCF_2Br$ | — | 109 |
| | | | $CF_2BrCF_2CHFBr$ | — | 110 |
| | $CH_2{=}CHCH_3$ | $Bz_2O_2$ | $CF_2BrCH_2CHBrCH_3$ | 55 | 108 |
| | $CHF{=}CHCH_3$ | $Bz_2O_2$ | $CF_2BrCHFCHBrCH_3$ | — | 109 |
| | $CH_3CH{=}CHCH_3$ | $Bz_2O_2$ | $CF_2BrCH(CH_3)CHBrCH_3$ | — | 108 |
| | $CH_3CH{=}CFCH_3$ | $Bz_2O_2$ | $CF_2BrCH(CH_3)CFBrCH_3$ | — | 109 |
| | $CH_2{=}CHCH_2OC_2H_5$ | $Bz_2O_2$ | $CF_2BrCH_2CHBrCH_2OC_2H_5$ | 31 | 75 |
| | $CH_2{=}CHCH_2OCF_2CHFCl$ | $Bz_2O_2$ | $CF_2BrCH_2CHBrCH_2OCF_2CHFCl$ | 46 | 75 |
| $CCl_2Br_2$ | $CH_2{=}CHCH_3$ | — | $CCl_2BrCH_2CHBrCH_3$ | — | 105 |
| | $CH_2{=}C(CH_3)_2$ | — | $CCl_2BrCH_2CBr(CH_3)_2$ | — | 105 |
| $CBr_4$ | $CH_2{=}CH_2$ | $hv$ | $CBr_3CH_2CH_2Br$ | — | 34 |
| | $CH_2{=}CHC_6H_{13}\text{-}n$ | $hv$ or $Ac_2O_2$ | $CBr_3CH_2CHBrC_6H_{13}\text{-}n$ | 96 | 34 |
| | $CH_2{=}CHC_6H_5$ | $hv$ | $CBr_3CH_2CHBrC_6H_5$ | 96 | 34 |
| | $CH_2{=}CHSi(Cl_2)CH_3$ | $hv$ | $CBr_3CH_2CHBrSi(Cl_2)CH_3$ | — | 83 |
| $CH_3CCl_2Br$ | $CH_2{=}CH_2$ | $Bz_2O_2$ | $CH_3CCl_2CH_2CH_2Br$ | (High) | 110 |
| $CF_2{=}CHI$ | $CH_2{=}CH_2$ | $hv$ | $CF_2{=}CHCH_2CH_2I$ | — | 111 |
| | $CH_2{=}CF_2$ | $hv$ | $CF_2{=}CHCH_2CF_2I$ | — | 111 |
| | $CF_2{=}CFCl$ | $hv$ | $CF_2{=}CHCF_2CFClI$ | — | 111 |
| $CF_2{=}CFI$ | $CH_2{=}CH_2$ | $hv$ | $CF_2{=}CFCH_2CH_2I$ | 67 | 112 |
| | $CH_2{=}CHF$ | $hv$ | $CF_2{=}CFCH_2CHFI$ | 50 | 112 |
| | $CH_2{=}CF_2$ | $hv$ | $CF_2{=}CFCH_2CF_2I$ | 24 | 112 |
| | $CF_2{=}CFI$ | $hv$ | $CF_2{=}CFCF_2CFI_2$ | 50 | 112 |
| | $CF_2{=}CHCl$ | $hv$ | $CF_2{=}CFCHClCF_2I$ | 4 | 112 |
| $CF_2{=}CClI$ | $CH_2{=}CH_2$ | $hv$ | $CF_2{=}CClCH_2CH_2I$ | — | 111 |
| $CCl_2{=}CCl_2$ | $CH_2{=}CH_2$ | $DTBP$ | $CCl_2{=}CClCH_2CH_2Cl$ | — | 113 |

| | | | | | |
|---|---|---|---|---|---|
| CF₂ClCOCH₂I | CH₂=CH₂ | hv | CF₂ClCOCH₂CH₂CH₂I | — | 111 |
| CF₂BrCFClBr | CH₂=CFCl | B₂O₃ | CF₂BrCFClCH₂CHFBr | 38 | 114 |
| | CHF=CF₂ | B₂O₃ | CF₂BrCFClCHFCF₂Br | 74 | 115 |
| | CH₂=CF₂ | B₂O₃ | CF₂BrCFClCF₂CH₂Br | 44 | 115 |
| | CH=CHCH₃ | B₂O₃ | CF₂BrCFClCH₂CHFBr | 16 | 115 |
| | CH=CHCH₂Cl | B₂O₃ | CF₂BrCFClCHFCH₂Cl | 83 | 114 |
| | CH=CHCH₂Cl | B₂O₃ | CF₂BrCFClCHClCH₂Cl | 45 | 114 |
| | CH=CHCl | B₂O₃ | CF₂BrCFClCHBrCH₂Cl | 33 | 114 |
| | CH₂=C(CH₃)₂ | B₂O₃ | CF₂BrCFClCH₂CBr(CH₃)₂ | 33 | 114 |
| | CH=CHCH₂CH₃ | B₂O₃ | CF₂BrCFClCHBrⁿC₃H₇ | 28 | 114 |
| | CH=CHClCH₂OC₂H₅ | B₂O₃ | CF₂BrCFClCHBrCH₂OC₂H₅ | 47 | 75 |
| | CH=CHCl(OCF₂CHFCl) | B₂O₃ | CF₂BrCFClCHBrOCF₂CHFCl | — | 34 |
| CF₂ClCFClI | CH₂=CH₂ | B₂O₃ | CF₂ClCFClCF₂I | 16 | 115 |
| | CHF=CF₂ | B₂O₃ | CF₂ClCFClCHFCFClI | 45 | 115 |
| | CH₂=CHCF₃ | B₂O₃ | CF₂ClCFClCHClCHF₃ | 79 | 115 |
| | CH=CHCF₃ | hv | CF₂ClCFClCH₂CHClCF₃ | 95 | 115 |
| | CH₂=CHS₂Cl₂F₅ | hv | CF₂ClCFClCH₂CHS₂Cl₂F₅ | 89 | 115 |
| | CH₂=CHS₂Cl₂F₅ | hv | CBr₂ClCH₂CHBrⁿC₃F₅ | 87 | 115 |
| CCl₂ClCH₂Br | CH₂=CH₂ | Thermal | CF₂ClCFClCF₂I | — | 83 |
| CBr₂ClCF₂I | CH=CH | — | CH₂BrCF₂ClCH₂CHBr | — | 83 |
| CF₂ClCF₂Cl | CH₂=CH₂ | B₂O₃ | ⁿ-C₃F₇CFClCF₂I | — | 83 |
| | CH=CH | — | ⁿ-C₃F₇CFClCF₂I | (High) | 110 |
| CF₂ClCF₂CF₃ | CH₂=CH₂ | — | (C₃F₇)₂CFCH₂CH₂I | 80 | 87 |
| CF₂CF₂CF₂CF₃ | CH₂=CCl₂ | — | (CF₂)₂CFCH₂CF₂I | 41 | 34 |
| CH₃Brⁿ(CH₂)₃CO₂H | Thermal | — | CH₃Br(CH₂)₃CO₂H₂CH₂Br | 18 | 100 |
| ⁿ-C₃F₇CClCF₂I₄ | CH=CH₂ | B₂O₃ | n-C₃F₇CFCl(CF₂)₂CFClCF₃ | 83 | 34 |
| | CH=CF₂ | — | | (High) | 99 |
| | | | | — | 99 |
| | | | | | 110 |
| | | | | | 100 |

*Note:* References 35 to 160 are on pp. 147–149.

TABLE IX

ADDITION OF ALDEHYDES

| Aldehyde | Unsaturated Compound | Initiator | Product | Yield, % Telomers | Refs. |
|---|---|---|---|---|---|
| Acetaldehyde | Ethylene | Per. or γ | $CH_3COC_2H_5$ | — | 116–118 |
| | Acetylene | Per. | $CH_2{=}CHCOCH_3$ | | 119 |
| | | | $CH_3COCH_2CH_2COCH_3$ | 11 | 120, 118 |
| | Propylene | Per. or γ | $CH_3COCH_2CH_2CH_3$ | — | 118 |
| | cis-2-Butene | γ | $CH_3COCH(CH_3)C_2H_5$ | — | 118 |
| | trans-2-Butene | γ | $CH_3COCH(CH_3)C_2H_5$ | — | 118 |
| | Isobutylene | γ | $CH_3COCH_2CH(CH_3)_2$ | 15 | 120 |
| | 1,5-Hexadiene | Per. | $CH_3CO(CH_2)_4CH{=}CH_2$ | 36 | 120 |
| | 1-Octene | Per. | $CH_3COC_8H_{17}$-n | 36 | 120 |
| | 1-Decene | Per. | $CH_3COC_{10}H_{21}$-n | 23 | 117, 120 |
| | 1-Dodecene | Per. | $CH_3COC_{12}H_{25}$-n | 63 | 121 |
| | Allyl acetate | Per. | $CH_3COCH_2CH_2CH_2OCOCH_3$ | 48 | 122 |
| | Acrolein diethyl acetal | Per. | $CH_3COCH_2CH_2CH(OC_2H_5)_2$ | 78 | 123 |
| | Diethyl maleate | Per. | $CH_3COCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ | 30 | 124 |
| | Methyl undecylenate | Per. | $CH_3CO(CH_2)_{10}CO_2CH_3$ | 31 | 125 |
| | Mesityl oxide | Per. | $CH_3CO(CH_2)_2CH_2COCH_3$ | 76 | 126 |
| | Perfluoropropylene | Per. | $CH_3COCF_2CFHCF_3$ | — | 118 |
| Propionaldehyde | Ethylene | γ | $C_2H_5COC_3H_7$ | | 118 |

| Reactant | Olefin | Product | Conditions | Telomers | References |
|---|---|---|---|---|---|
| n-Butyraldehyde | Ethylene | $n\text{-}C_3H_7COC_2H_5$ | Per. | | 116 |
| | Isobutylene | $n\text{-}C_3H_7COCH_2CH(CH_3)_2$ | Per. | 30 | 120 |
| | 1-Hexene | $n\text{-}C_3H_7COC_6H_{13}\text{-}n$ | Per. | 41 | 127 |
| | Cyclohexene | $COC_3H_7\text{-}n$ | Per. | Low | 120 |
| | 1-Octene | $n\text{-}C_3H_7COC_8H_{17}\text{-}n$ | Per. | 57 | 127 |
| | 1-Dodecene | $n\text{-}C_3H_7COC_{12}H_{25}\text{-}n$ | Per. | — | 117 |
| | Acrolein diethyl acetal | $n\text{-}C_3H_7COCH_2CH_2CH(OC_2H_5)_2$ | Per. | 28 | 121 |
| | Methyl acrylate | $n\text{-}C_3H_7COCH_2CH_2CO_2CH_3,\ n$ | Per. | 11 | 124 |
| | Allyl acetate | $n\text{-}C_3H_7COCH_2CH_2CH_2O_2CCH_3,\ n$ | Per. | 63 | 121 |
| | Diethyl fumarate | $n\text{-}C_3H_7COCH(CO_2C_2H_5)CH_2CO_2C_2H_5,\ n$ | Per. | 70 | 123, 124 |
| | Dimethyl maleate | $n\text{-}C_3H_7COCH(CO_2CH_3)CH_2CO_2CH_3,\ n$ | Per. | 26 | 123, 124 |
| | 3-Penten-2-one | $n\text{-}C_3H_7COCH(CH_3)CH_2COCH_3$ | Per. | 64 | 125 |
| | Methyl isopropenyl ketone | $n\text{-}C_3H_7COCH_2CH(CH_3)COCH_3$ | Per. | — | 128 |
| | 5-Hexen-2-one | $n\text{-}C_3H_7CO(CH_2)_4COCH_3$ | Per. | 71 | 128 |
| | Mesityl oxide | $n\text{-}C_3H_7COC(CH_3)_2CH_2COCH_3$ | Per. | 60–100 | 125 |
| | Phorone | $n\text{-}C_3H_7COCH(CH_3)_2CH_2COCH=C(CH_3)_2$ | Per. | 80 | 125 |
| | 3-Hexen-2-one | $n\text{-}C_3H_7COCH(C_2H_5)CH_2COCH_3$ | Per. | 42 | 125 |
| | Crotonophenone | $n\text{-}C_3H_7COCH(CH_3)CH_2COC_6H_5,\ n$ | Per. | 24 | 125 |
| | 3,3-Diphenyl-1-butene | $n\text{-}C_3H_7COCH_2CH_2C(C_6H_5)_2CH_3$ | Per. | — | 15 |
| | Perfluoropropylene | $n\text{-}C_3H_7COCF_2CHFCF_3$ | Per. | 70 | 126 |

TABLE IX—Continued

ADDITION OF ALDEHYDES

| Aldehyde | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| Isobutyraldehyde | Ethylene | $\gamma$ | $(CH_3)_2CHCOC_2H_5$ | — | 118 |
|  | 1-Octene | Per. | $(CH_3)_2CHCOC_8H_{17}$-$n$ | Low | 120 |
| Trimethylacetaldehyde | Ethylene | $\gamma$ | $(CH_3)_3CCOC_2H_5$ | — | 118 |
| $n$-Heptanal | 1-Octene | Per. | $n$-$C_6H_{13}COC_8H_{17}$-$n$ | 75 | 127 |
|  | Cyclohexene | Per. |  $COC_6H_{13}$-$n$ | Low | 127 |
|  | Vinyl cyclohexene | Per. | $CH_3CH_2COC_6H_{13}$-$n$  | 21 | 120 |
|  | Mesityl oxide | Per. | $n$-$C_6H_{13}COC(CH_3)_2CH_2COCH_3$ | 61 | 125 |
| 2-$n$-Propylpentanal | Diethyl maleate | Per. | $n$-$C_6H_{13}COCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ | 76 | 123 |
|  | Diethyl maleate | Per. | $(n$-$C_3H_7)_2CHCOCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ | 59 | 123 |
| $\beta$-Methoxypropionaldehyde | Diethyl maleate | Per. | $CH_3OCH_2CH_2COCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ | 55 | 123 |
| Glutaraldehyde | Diethyl maleate | Per. | $CH_2[CH_2COCH(CO_2C_2H_5)CH_2CO_2C_2H_5]_2$ | 100 | 123 |
| Benzaldehyde | Diethyl maleate | Per. | $C_6H_5COCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ | 5 | 123 |
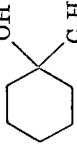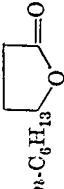
Note: References 35 to 160 are on pp. 147–149.

TABLE X

ADDITION OF ALCOHOLS

| Alcohol | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| Methanol | 1-Octene | DTBP | $n\text{-}C_6H_{13}CH_2OH$ | 14 | 29 |
| | Perfluoroethylene | $B_2O_4$ | $CHF_2CF_2CH_2OH$ | | 126 |
| | Perfluoropropylene | $B_2O_4$ | $CF_3CHFCF_2CH_2OH$ | 75 | 126 |
| | Perfluoro-1-butene | $B_2O_4$ | $C_2F_5CHFCF_2CH_2OH$ | 72 | 126 |
| | Perfluoro-2-butene | $B_2O_4$ | $CF_3CHFCHFCF_2CH_2OH$ | 95 | 126 |
| | Perfluoro-1-pentene | $B_2O_4$ | $n\text{-}C_3F_7CHFCF_2CH_2OH$ | 89 | 126 |
| | Perfluoro-1-heptene | $BzO_2$ | $n\text{-}C_5F_{11}CHFCF_2CH_2OH$ | 23 | 126 |
| Ethanol | Ethylene | DTBP | $CH_3CH_2CHOHCH_3$ | 10 | 29 |
| | 1-Hexene | $h\nu$ | $n\text{-}C_6H_{13}CHOHCH_3$ | 19 | 29 |
| | 1-Octene | DTBP | $n\text{-}C_8H_{17}CHOHCH_3$ | 13 | 29 |
| | Perfluoro-1-butene | $B_2O_4$ | $C_2F_5CHFCF_2CHOHCH_3$ | 38 | 126 |
| | Perfluoro-1-pentene | $B_2O_4$ | $n\text{-}C_3F_7CHFCF_2CHOHCH_3$ | 70 | 126 |
| | Allyl alcohol | DTBP | $HO(CH_2)_3CHOHCH_3$ | 30 | 29 |
| 2-Propanol | Ethylene | DTBP | $CH_3CH_2C(CH_3)_2OH$ | | 29 |
| | Propylene | DTBP | $n\text{-}C_3H_7C(CH_3)_2OH$ | 46 | 29 |
| | 1-Octene | DTBP | $n\text{-}C_8H_{17}C(CH_3)_2OH$ | 51 | 29 |
| | 1-Dodecene | DTBP | $n\text{-}C_{12}H_{25}C(CH_3)_2OH$ | 40 | 29 |
| | Perfluoro-1-pentene | $B_2O_4$ | $n\text{-}C_3F_7CHFCF_2C(CH_3)_2OH$ | 37 | 126 |
| 1-Butanol | 1-Octene | DTBP | $n\text{-}C_8H_{17}CHOHC_3H_7\text{-}n$ | 57 | 29 |
| 2-Butanol | 1-Octene | DBP | $n\text{-}C_8H_{17}C(OH)(CH_3)C_2H_5$ | | 29 |
| 1-Pentanol | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}CHOHC_4H_9\text{-}n$ | | 29 |
| 1-Hexanol | 1-Octene | DTBP | $n\text{-}C_8H_{17}CHOHC_5H_{11}\text{-}n$ | | 128 |
| | 1-Tridecene | DTBP | $n\text{-}C_{13}H_{27}CHOHC_5H_{11}\text{-}n$ | | 128 |
| | 1-Octene | DBP | $n\text{-}C_8H_{17}CHOHC_5H_{11}\text{-}n$ | | 128 |
| | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}CHOHC_5H_{11}\text{-}n$ | | 128 |
| Cyclohexanol | 1-Hexene | DTBP | cyclo-$C_6H_{10}(OH)(C_6H_{13}\text{-}n)$ | 42 | 29 |

Note. References 35 to 160 are on pp. 147–149.

TABLE X—*Continued*

ADDITION OF ALCOHOLS

| Alcohol | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| Cyclohexanol (cont.) | 1-Octene | DTBP |  | — | 29 |
| | Acrylic acid | DTBP |  | — | 129 |
| 1-Heptanol | 1-Hexene | DTBP | $(n\text{-}C_6H_{13})_2CHOH$ | — | 128 |
| | Acrylic acid | DTBP |  | — | 129 |
| | Methyl acrylate | DTBP |  | — | 129 |
| 1-Octanol | 1-Hexene | DTBP | $n\text{-}C_6H_{13}CHOHC_7H_{15}\text{-}n$ | — | 128 |
| | 1-Heptene | DTBP | $(n\text{-}C_7H_{15})_2CHOH$ | — | 128 |
| | 1-Nonene | DTBP | $n\text{-}C_9H_{19}CHOHC_7H_{15}\text{-}n$ | — | 128 |
| 2-Octanol | Acrylic acid | DTBP |  | — | 129 |
| 2-Ethyl-1-hexanol | Acrylic acid | DTBP | $n\text{-}C_4H_9CH(C_2H_5)$  | — | 129 |
| 1-Nonanol | 1-Hexene | DTBP | $n\text{-}C_6H_{13}CHOHC_8H_{17}\text{-}n$ | — | 128 |
| | 1-Heptene | DTBP | $n\text{-}C_7H_{15}CHOHC_8H_{17}\text{-}n$ | — | 128 |
| 1-Decanol | Methyl acrylate | DTBP |  | — | 129 |
| | 1-Hexene | DTBP | $n\text{-}C_6H_{13}CHOHC_9H_{19}\text{-}n$ | — | 128 |
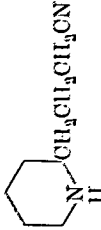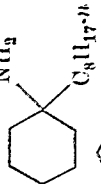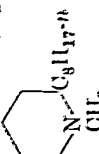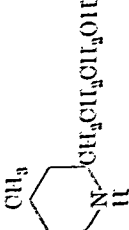
*Note:* References 35 to 160 are on pp. 147–149.

TABLE XI

ADDITION OF AMINES

| Amine | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| Isopropylamine | 1-Octene | DTBP | $(CH_3)_2C(NH)C_8H_{17}$-n | 46 | 130 |
| n-Butylamine | 1-Octene | DTBP, $h\nu$ | n-$C_4H_9CH(NH_2)C_8H_{17}$-n | 36 | 130 |
| Pyrrolidine | Allyl alcohol | DTBP | $\overset{\displaystyle N-CH_2CH_2CH_2OH}{\underset{H}{\big|}}$ | 63 | 130 |
| Piperidine | Ethylene | DTBP | $N-C_2H_5$ (piperidine) | — | 130 |
|  | Propylene | DTBP | $N-C_3H_7$-n (piperidine) | — | 130, 131 |
|  | 1-Hexene | DTBP | $N-C_4H_9$-n (piperidine) | 60 | 130 |
|  | 1-Octene | DTBP, $h\nu$ | $N-C_8H_{17}$-n (piperidine) | 70 | 130, 131 |

*Note:* References 35 to 160 are on pp. 147–149.

TABLE XI—*Continued*

ADDITION OF AMINES

| Amine | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| Piperidine (cont.) | Allyl alcohol | DTBP | N—CH$_2$CH$_2$CH$_2$OH (piperidine, N—H) | 54 | 130 |
| | Allyl cyanide | DTBP | N—CH$_2$CH$_2$CH$_2$CN (piperidine, N—H) | 48 | 130 |
| n-Hexylamine | 1-Octene | DTBP | n-C$_5$H$_{11}$CH(NH$_2$)C$_8$H$_{17}$-n | 36 | 130 |
| Cyclohexylamine | 1-Octene | DTBP | cyclohexane with NH$_2$ and C$_8$H$_{17}$-n | 55 | 130 |
| N-Methylpiperidine | 1-Octene | DTBP | N—C$_8$H$_{17}$-n, CH$_3$ (piperidine) | 22 | 130 |
| γ-Pipecoline | Allyl alcohol | DTBP | N—CH$_2$CH$_2$CH$_2$OH, CH$_3$ (piperidine, N—H) | 42 | 130 |

*Note:* References 35 to 100 are on pp. 147–149.

TABLE XII

ADDITION OF FORMIC ACID DERIVATIVES

| Addend | Unsaturated Compound | Initiator | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| Methyl formate | Ethylene | DTBP | $C_2H_5CO_2CH_3$ | Telomers | 132, 133 |
| | Propylene | DTBP | $n\text{-}C_4H_9CO_2CH_3$ | Telomers | 133 |
| | 1-Hexene | DTBP | $n\text{-}C_7H_{15}CO_2CH_3$ | 20 | 132 |
| | Cyclohexene | DTBP | ⬡—$CO_2CH_3$ | 36 | 134 |
| | 1-Octene | DTBP | $n\text{-}C_9H_{19}CO_2CH_3$ | 13 | 134 |
| | 1-Decene | DTBP | $n\text{-}C_{11}H_{23}CO_2CH_3$ | 21 | 134 |
| | 1-Dodecene | DTBP | $n\text{-}C_{13}H_{27}CO_2CH_3$ | 18 | 134 |
| Ethyl formate | Ethylene | DTBP | $C_3H_7CO_2C_2H_5$, and $HO_2CH(C_3H_7)C_2H_5$ | Telomers | 132 |
| N,N-Dimethyl-formamide | 1-Octene | DTBP | $n\text{-}C_9H_{19}CON(CH_3)_2$ | 60 | 135 |
| N-Butyl-formamide | 1-Octene | DTBP | $n\text{-}C_9H_{17}CONHC_4H_9\text{-}n$ | 40 | 135 |
| | Methyl 10-undecylenate | DTBP | $n\text{-}C_4H_9NHCO(CH_2)_{10}CO_2CH_3$ and $CH_3O_2C(CH_2)_{10}CONHC(CH_3)_3$ | 77 61 | 135 135 |

Note: References 35 to 160 are on pp. 147-149.

TABLE XIII

ADDITION OF ESTERS AND ACIDS

| Addend | Unsaturated Compound | Initiator | Product (Esters) | Yield, % | Refs. |
|---|---|---|---|---|---|
| $CH_3CO_2CH_3$ | 1-Octene | DTBP | $n\text{-}C_9H_{19}CO_2CH_3$ | 11 | 134 |
| $BrCH_2CO_2C_2H_5$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBr(CH_2)_2CO_2C_2H_5$ | 48 | 136 |
| $Cl_2CHCO_2C_2H_5$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_8H_{17}CCl_2CO_2C_2H_5$ | 40 | 137 |
| $CH_3CHBrCO_2C_2H_5$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2CH(CH_3)CO_2C_2H_5$ | 64 | 136 |
| $CH_3CHBrCO_2C_4H_9\text{-}t$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2CH(CH_3)CO_2C_4H_9\text{-}t$ | 49 | 136 |
| $NCCH_2CO_2CH_3$ | 1-Octene | DTBP | $n\text{-}C_6H_{13}CHCNCO_2CH_3$ | 69 | 134 |
| $NCCH_2CO_2C_2H_5$ | 1-Octene | DTBP | $n\text{-}C_8H_{17}CHCNCO_2C_2H_5$ | — | 138 |
| $CH_2(CO_2CH_3)_2$ | Ethylene | DTBP | $C_2H_5CH(CO_2CH_3)_2$ | 16 | 30 |
|  | Propylene | DTBP | $n\text{-}C_3H_7CH(CO_2CH_3)_2$ | — | 30 |
|  | 1-Hexene | DTBP | $n\text{-}C_6H_{13}CH(CO_2CH_3)_2$ | 17 | 134 |
|  | 1-Octene | DTBP | $n\text{-}C_8H_{17}CH(CO_2CH_3)_2$ | 76 | 30 |
|  | Vinyl acetate | DTBP | $CH_3CO_2(CH_2)_3CH(CO_2CH_3)_2$ | 64 | 30 |
|  | Allyl acetate | DTBP | $CH_3CO_2(CH_2)_3CH(CO_2CH_3)_2$ | 26 | 30 |
| $CH_2(CO_2C_2H_5)_2$ | 1-Octene | DTBP | $n\text{-}C_8H_{17}CH(CO_2C_2H_5)_2$ | 28 | 30, 138 |
|  | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}CH(CO_2C_2H_5)_2$ | 75 | 139 |
|  | 4-Methyl-1-decene | DTBP | $n\text{-}C_6H_{13}CH(CH_3)CH_2CH(CO_2C_2H_5)_2$ | 68 | 139 |
| $CHBr(CO_2C_2H_5)_2$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBrCH(CO_2C_2H_5)_2$ | 58 | 136 |
| $CCl_2(CO_2C_2H_5)_2$ | Ethylene | $Bz_2O_2$ | $CH_2ClCH_2CCl(CO_2C_2H_5)_2$ | Telomers | 140 |
| $C_2H_5CHBrCO_2C_2H_5$ | 1-Octene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2CH(C_2H_5)CO_2C_2H_5$ | 47 | 136 |
| $(CH_3)_2CBrCO_2C_2H_5$ | Ethylene | $Ac_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2C(CH_3)_2CO_2CH_3$ | 24 | 136 |
| $CH_3COCH_2CO_2CH_3$ | 1-Hexene | DTBP | $CH_3COCH(C_6H_{13}\text{-}n)CO_2CH_3$ | — | 134 |
|  | Cyclohexene | DTBP | $CH_3COCH(C_6H_{11})CO_2CH_3$ | 45 | 134 |
|  | 1-Octene | DTBP | $CH_3COCH(C_8H_{17}\text{-}n)CO_2CH_3$ | 8 | 134 |
|  | 1-Decene | DTBP | $CH_3COCH(C_{10}H_{21}\text{-}n)CO_2CH_3$ | 46 | 134 |
| $CH_3COCCl_2CO_2C_2H_5$ | 1-Octene | DTBP | $CH_3COCCl(C_8H_{17}\text{-}n)CO_2C_2H_5$ | 64 | 134 |
| $CH_3COCCl_2CO_2C_2H_5$ | 1-Octene | DTBP | $CH_3COCCl(C_8H_{17}\text{-}n)CO_2C_2H_5$ | 82 | 30, 138 |
|  | 1-Octene | $Bz_2O_2$ | $CH_3COCCl(CH_2CHClC_6H_{13}\text{-}n)CO_2C_2H_5$ | 28 | 140 |
| $\begin{array}{c}CH_2CO_2CH_3\\ \mid\\ CH_2CO_2CH_3\end{array}$ | 1-Octene | DTBP | $\begin{array}{c}n\text{-}C_8H_{17}CHCO_2CH_3\\ \mid\\ CH_2CO_2CH_3\end{array}$ | 67 | 139 |

| | | | | | |
|---|---|---|---|---|---|
| CH₃CH₂CH₂CH₃ | DTBP | 1 Octene | CH₃CH₂CHC₈H₁₇-n | 61 | 30 |
| C₂H₅CH(CO₂C₂H₅)₂ | DTBP | 1-Hexene | n-C₄H₉C₂H₅CH(CO₂C₂H₅)₂, b | 74 | 30 |
| | DTBP | 1 Octene | C₂H₅C(C₈H₁₇)(CO₂C₂H₅)₂-n | 60 | 134 |
| CH₃CHClCH₂CH₃ | DTBP | 1-Octene | CH₃CHClCH₂CH₃, n | 62 | 30 |
| CH₂(CHCO₂CH₃) ·CO | DTBP | 1-Octene | Cl₂CCH₂CH=CHCO₂CH₃ | 80 | 82 |
| Cl₃CCHClCO₂CH₃ | | | | | |
| BrCH₂CO₂CH₃ | DTBP | 1-Octene | n-C₈H₁₇CH₂CHCO₂CH₃ | 42 | 139 |
| CH₃CO₂CH₃ | | | CH₃ | | |
| CH₄ | DTBP | 1-Decene | CH₃CO₂CH₃ | 38 | 139 |
| CH₃CH₂CO₂CH₃ | | | CH₃ | | |
| CH₃CO₂CH₃ | DTBP | 1-Octene | n-C₈H₁₇CH(CO₂CH₃)CH₃ | 52 | 139 |
| (CH₃)₃ | | | (CH₃)₃ | | |
| CH₃CO₂CH₃ | DTBP | 1-Octene | CH₃CO₂CH₃ | | 139 |
| CH₃CO₂CH₃ | | | n-C₈H₁₇CH₂CO₂CH₃ | | |
| (CH₃)₄ | DTBP | 1-Octene | (CH₃)₄ | 55 | 139 |
| CH₃CO₂CH₃ | | | CH₃CO₂CH₃ | | |

*Note* References 35 to 160 are on pp. 147–149.

TABLE XIII—*Continued*

ADDITION OF ESTERS AND ACIDS

| Addend | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| | | | *Esters* | | |
| $n\text{-}C_9H_{19}CO_2CH_3$ | $n\text{-}C_7H_9OCH{=}CH_2$ | DTBP | $n\text{-}C_7H_9OCH_2CH_2CH(C_8H_{17}\text{-}n)CO_2CH_3$ | 60–75 | 141 |
| | $(CH_3)_3SiCH{=}CH_2$ | DTBP | $(CH_3)_3SiCH_2CH_2CH(C_8H_{17}\text{-}n)CO_2CH_3$ | 60–75 | 141 |
| | $(C_2H_5)_2(CH_3)SiCH{=}CH_2$ | DTBP | $(C_2H_5)_2(CH_3)SiCH_2CH_2CH(C_8H_{17}\text{-}n)CO_2CH_3$ | 60–75 | 141 |
| | Methyl acrylate | DTBP | $CH_3O_2CCH_2CH_2CH(C_8H_{17}\text{-}n)CO_2CH_3$ | 18 | 139 |
| | | | *Acids* | | |
| Propionic | 1-Octene | DTBP | $n\text{-}C_8H_{17}CH(CH_3)CO_2H$ | 60–75 | 141 |
| | 1-Tridecene | DTBP | $n\text{-}C_{13}H_{27}CH(CH_3)CO_2H$ | 60–75 | 141 |
| $n\text{-}C_3H_7CO_2H$ | $n\text{-}C_7H_{15}OCH_2CH{=}CH_2$ | DTBP | $n\text{-}C_7H_{15}OCH_2CH_2CH_2CH(CH_3)CO_2H$ | 60–75 | 141 |
| | 1-Hexene | DTBP | $n\text{-}C_6H_{13}CH(C_2H_5)CO_2H$ | 60–75 | 141 |
| | Vinyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH(C_2H_5)CO_2H$ | 37–52 | 142 |
| | Allyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH_2CH(C_2H_5)CO_2H$ | 37–52 | 142 |
| $(CH_3)_2CHCO_2H$ | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}C(CH_3)_2CO_2H$ | 60–75 | 141 |
| $n\text{-}C_4H_9CO_2H$ | Vinyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH(C_3H_7\text{-}n)CO_2H$ | 37–52 | 142 |
| | $n\text{-}C_{10}H_{21}OCH_2CH{=}CH_2$ | DTBP | $n\text{-}C_{10}H_{21}OCH_2CH_2CH_2CH(C_3H_7\text{-}n)CO_2H$ | 60–75 | 141 |
| | $CH_3O_2C(CH_2)_8CH{=}CH_2$ | DTBP | $CH_3O_2C(CH_2)_{10}CH(C_3H_7\text{-}n)CO_2H$ | 60–75 | 141 |
| $n\text{-}C_5H_{11}CO_2H$ | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}CH(C_4H_9\text{-}n)CO_2H$ | 60–75 | 141 |
| $n\text{-}C_6H_{13}CO_2H$ | 2-Ethyl-1-hexene | DTBP | $(n\text{-}C_4H_9)(C_2H_5)CHCH_2CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| | 1-Nonene | DTBP | $n\text{-}C_9H_{19}CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| | 1-Decene | DTBP | $n\text{-}C_{10}H_{21}CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| | 5-Ethyl-1-nonene | DTBP | $(n\text{-}C_4H_9)(C_2H_5)CH(CH_2)_3CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| | 4-Methyl-1-decene | DTBP | $(n\text{-}C_6H_{13})(CH_3)CH(CH_2)_2CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| | Vinyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH(C_5H_{11}\text{-}n)CO_2H$ | 37–52 | 142 |
| | Methyl acrylate | DTBP | $CH_3O_2CCH_2CH_2CH(C_5H_{11}\text{-}n)CO_2H$ | 18 | 139 |
| | Allyl octyl ether | DTBP | $n\text{-}C_8H_{17}OCH_2CH_2CH_2CH(C_5H_{11}\text{-}n)CO_2H$ | 60–75 | 141 |
| $n\text{-}C_7H_{15}CO_2H$ | 1-Octene | DTBP | $n\text{-}C_8H_{17}CH(C_6H_{13}\text{-}n)CO_2H$ | 60–75 | 141 |
| | Vinyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH(C_6H_{13}\text{-}n)CO_2H$ | 37–52 | 142 |
| | Allyl acetate | DTBP | $CH_3CO_2CH_2CH_2CH_2CH(C_6H_{13}\text{-}n)CO_2H$ | 37–52 | 142 |
| $n\text{-}C_8H_{17}CO_2H$ | Allyl formate | DTBP | $HCO_2CH_2CH_2CH_2CH(C_7H_{15}\text{-}n)CO_2H$ | 37–52 | 142 |

*Note:* References 35 to 160 are on pp. 147–149.

TABLE XIV

ADDITION OF ETHERS AND ACETALS

| Addend | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| $(C_4H_9)_2O$ | Perfluoroethylene | $Bz_2O_2$ | $C_4H_9OCH(CH_3)CF_2CHF_2$ | — | 143 |
| $i\text{-}C_3H_7O$ | 1-Octene | $D_2P$ | $n\text{-}C_6H_{13}CH(CH_3\text{-}n)C_3H_7, n$ | — | 144 |
| $(CH_3)_2O$ | Perfluoroethylene | $Bz_2O_2$ | | Telomers | 143 |
| $CH_3[OCH]_4$ | Perfluoroethylene | $Bz_2O_2$ | $(CH_3O)_2CHCH_2\cdots$ | 36 | 143 |
| | Maleic anhydride | $Bz_2O_2$, or $hv$ | | | 145 |
| $CH_3[OC_4H_9\text{-}n]_4$ | Dimethyl maleate | $Bz_2O_2$ | $C_4H_9OCH_2OCH(C_4H_9)CH_2CO_2CH_3$ / $CH_2CO_2CH_3$ | — | 146 |
| $CH_3[OC_2H_5\text{-}n]_4$ | Dimethyl maleate | $Bz_2O_2$ | $(n\text{-}C_4H_9O)_2CHCH(CO_2CH_3)$ / $CH_2CO_2CH_3$ | — | 147 |
| $CH_3[OC_2H_5]_4$ | Dimethyl maleate | $Bz_2O_2$ | $(C_2H_5O)_2CH[CH(CO_2CH_3)]CH_2CO_2CH_3$ / $CH_2CO_2CH_3$ | — | 147 |
| | Diethyl maleate | — | $(C_2H_5O)_2CH[CH(CO_2C_2H_5)]CH_2CO_2C_2H_5$ / $CH_2CO_2C_2H_5$ | — | 148 |
| | Diethyl fumarate | — | $(C_2H_5O)_2CH[CH(CO_2C_2H_5)]CH_2CO_2C_2H_5$ / $CH_2CO_2C_2H_5$ | — | 148 |
| | Di-2-ethylhexyl maleate | — | $(C_2H_5O)_2CH[CH(CO_2CH_2CH(C_2H_5)C_4H_9\text{-}n]CH_2CO_2CH_2CH(C_2H_5)C_4H_9\text{-}n$ | — | 148 |

*Note:* References 25 to 160 are on pp 147–149.

TABLE XIV—*Continued*

ADDITION OF ETHERS AND ACETALS

| Addend | Unsaturated Compound | Initiator | Product | Yield, % | Refs. |
|---|---|---|---|---|---|
| $CH_3CH(OC_2H_5)_2$ (cont.) | Diethyl itaconate | — | $(C_2H_5O)_2C(CH_3)CH_2CHCO_2C_2H_5$<br>$CH_2CO_2C_2H_5$ | — | 148 |
| | Tri-n-butyl aconitate | — | $(C_2H_5O)_2C(CH_3)CHCO_2C_4H_9\text{-}n$<br>$CHCO_2C_4H_9\text{-}n$<br>$CH_2CO_2C_4H_9\text{-}n$ | — | 149 |
| | Dimethyl maleate | $Bz_2O_2$ | $(C_2H_5O)_3CCCHCO_2CH_3$<br>$CH_2CO_2CH_3$ | — | 148 |
| $CH_2CH_2CH_2CH_2{-}O$ (ring) | Ethylene | Thermal | $CH_3CH_2CH_2CH_2CH_2CH_5$ (tetrahydrofuran ring) | 21 | 149 |
| | 1-Octene | DTBP | $n\text{-}C_8H_7COC_8H_{17}\text{-}n$<br>$CH_2CH_3$ (ring) | — | 150 |
| $CH_2CH_2$ $O$ $CH_2CH_2$ $O$ (1,4-dioxane ring) | Perfluoroethylene | $Bz_2O_2$ | $CH_2CH$ (ring) $CF_2CHF_2$ | — | 143 |
| | Perfluoroethylene | $Bz_2O_2$ | $C_5H_6F_4O_2$ | — | 143 |
| 2-Methyl-2-chloromethyl-1-3-dioxane $CH_2CH_2$ $CH_2$ $O$ $CH_2{-}O$ | Perfluoroethylene | $Bz_2O_2$ | $C_6H_{11}F_4ClO_2$ | — | 143 |

*Note:* References 35 to 160 are on pp. 147–149.

TABLE XV

MISCELLANEOUS ADDITIONS

| Addend | Unsaturated Compound | Initiator | Product(s) | Yield, % | Refs. |
|---|---|---|---|---|---|
| Methane | Ethylene | $Co^{60}$ | $CH_3CH_2CH_3$ and other hydrocarbons | — | 151 |
| Propane | Acetylene | $Co^{60}$ | $(CH_3)_2CHCH=CH_2$ | — | 152 |
| Isobutane | Ethylene | Thermal | $(CH_3)_3CCH_2CH_3$ | 40 | 153 |
|  | Propylene | $Co^{60}$ | $(CH_3)_3CCH_2CH_2CH_3$ | — | 154 |
| Cyclopentane | Formaldehyde | DTBP | $C_5H_9CH_2OH$ | 38 | 155 |
| Cyclohexane | Formaldehyde | DTBP | $C_6H_{11}CH_2OH$ | 21.4 | 155 |
| Toluene | Ethylene | DTBP | $C_6H_5CH_2CH_2CH_2CH_3$, and other alkylbenzenes | — | 156 |
| p Xylene | 1-Hexene | DTBP | $p\text{-}CH_3C_6H_4C_8H_{17}$ | 25 | 156 |
| $Br_2CNO_2$ | 1-Hexene | $Bz_2O_2$ | $n\text{-}C_4H_9CHBrCH_2CBr_2NO_2$ | 51 | 157 |
|  | Cyclohexene | $Bz_2O_2$ |  | — | 157 |
|  | 1-Heptene | $Bz_2O_2$ | $n\text{-}C_5H_{11}CHBrCH_2CBr_2NO_2$ | 57 | 157 |
|  | 1-Octene | $Bz_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2CBr_2NO_2$ | 73 | 157 |
|  | 6-Methyl-1-heptene | $Bz_2O_2$ | $(CH_3)_2CH(CH_2)_3CHBrCH_2CBr_2NO_2$ | 49 | 157 |
| $CH_2BrCN$ | 1-Octene | $Bz_2O_2$ | $n\text{-}C_6H_{13}CHBrCH_2CH_2CN$ | 66 | 158 |
| $CHBr_2CN$ | Allyl acetate | $Bz_2O_2$ | $CH_3CO_2CH_2CHBrCH_2CHBrCN$ | 52 | 158 |

Note: References 35 to 160 are on pp. 147–149.

## REFERENCES FOR TABLES V–XV

[35] Hanford and Joyce, U S pat 2,440,800 [C A, 42, 6373 (1948)]

[36] Harmon, Ford, Hanford, and Joyce, J Am Chem Soc, 72, 2213 (1950)

[37] Freidina and Belyavskiĭ, Izv Akad Nauk SSSR, Otd Khim Nauk, 1961, 177 (1961) [C A, 55, 19754 (1951)]

[38] Sladkov, Berlin, Sergeev, and Sladkova, Khim Nauka s Promy, 2, 669 (1957) [C A, 52, 8143 (1958)]

[39] Lewis and Mayo, J. Am Chem. Soc, 75, 457 (1954).

[40] Topchev, Bogomolova, and Golffarb, Doklady Akad Nauk SSSR, 107, 420 (1956) [C A, 50, 14503 (1956)]

[41] Peterson, U S pat 2,401,099 [C A, 40, 4907 (1946)]

[42] Kooyman and Farenhorst, Rec Trav Chim, 70, 867 (1951)

[43] Israelashvili and Shabatay, J Chem Soc, 1951, 3261

[44] Dupont, Dulou, and Figere˘, Compt Rend, 242, 628 (1956)

[45] Greene and Rees, J Am Chem Soc, 82, 893 (1961).

[46] Kharasch, Jensen, and Urry, Science, 102, 128 (1945).

[47] Dupont, Dulou, and Clement, Bull Soc Chim France, 1951, 1002

[48] Clement, Compt Rend, 232, 2016 (1951)

[49] Israelashvili and Diamant, J Am. Chem Soc, 74, 3185 (1952).

[50] Dupont, Dulou, and Clement, Compt Rend, 236, 2512 (1953)

[51] Oldroyd, Fisher, and Goldblatt, J Am Chem Soc, 72, 2407 (1950).

[52] Dupont, Dulou, and Clement, Bull Soc Chim France, 1950, 1056, 1115.

[53] Quelet and Durand Drant, Compt Rend, 246, 774 (1958)

[54] Harmon, U S pat 2,396,261 [C A, 40, 3466 (1946)]

[55] Patrick, U S pat 2,676,981 [C A, 49, 5510 (1955)]

[56] Shostakovskii, Bogomolova, Zverov, and Plotnikova, Izv Akad. Nauk SSSR, Otd Khim Nauk, 1956, 1236 [C A, 51, 5730 (1957)]

[57] Bogdanova and Shostakovskii, Izv Akad Nauk SSSR, Otd Khim. Nauk, 1957, 235 [C A, 52, 15418 (1958)]

[58] Shostakovskii, Bogdanova, Plotnikova, and Dubrova, Izv Akad. Nauk SSSR, Otd. Khim Nauk, 1958, 756 [C A, 52, 19908 (1958)]

[59] Hall and Jacobs, J. Chem Soc, 1954, 2034

[60] Borsov, Izv Akad Nauk SSSR, Otd. Khim. Nauk, 1951, 524 [C A., 46, 7054 (1952)].

[61] Matteson, J Am Chem Soc, 81, 5004 (1959)

[62] Kharasch, Freiman, and Urry, J. Org Chem, 13, 570 (1948).

[63] Skinner, Bishop, Tetzen, and Johnston, J Org Chem, 23, 1710 (1958)

[64] Skell and Woodworth, J Am Chem Soc, 72, 4638 (1955)

[65] Kharasch and Sage, J Org Chem, 14, 537 (1949)

[66] Kharasch, Simon, and Nudenberg, J. Org-Chem, 18, 328 (1953).

[67] Kharasch and Friedlander, J Org Chem, 14, 239 (1949)

[68] Herba and Anderson, J Am. Chem Soc, 72, 4940 (1937)

[69] Kharasch, Jerome, and Urry, J. Org Chem, 15, 966 (1950).

[70] Kharasch and Sage, J Org Chem, 14, 537 (1949)

[71] Henne and Kraus, J Am. Chem Soc, 76, 1175 (1954)

[72] Henne and Nager, J. Am. Chem Soc, 73, 5527 (1951)

[73] Haszeldine, J. Chem Soc, 1953, 3565

[74] Tarrant, Brey, and Gray, J. Am. Chem Soc, 80, 1711 (1958).

[75] Tarrant and Stump, J. Org Chem, 26, 4646 (1961)

[76] W. S. Nyrdinsgler, Am Chem Soc Meeting at Paris (Spring 1958), p. 18N

[77] Bengough and Thomson, Trans. Chem. & Ind. (London). 1957, 426.

[78] Bengough and Thomson, Trans Faraday Soc, 56, 407 (1960)

[79] Ladd, U S pat 2,554,533 [C A, 45, 9556 (1951)]

[80] Huang, J. Chem Soc, 1956, 1719

[81] Kharasch, U S. pat, 2,485,099 [C A, 44, 8430 (1950)].

[132] Petrov, Nikushin, and Vorob ev, *Fette, Seifen, Anstrichmittel*, 59, 1023 (1957) [C A , 53, 1127 (1959)]

[133] E S Huyser, Ph D Thesis, University of Chicago, 1954

[134] Friedman and Shechter, *Tetrahedron Letters*, 1961, 238

[135] Kharasch, Skell, and Fisher, *J Am Chem Soc*, 70, 1055 (1948)

[136] Kharasch, Urry, and Jensen, *J Am Chem Soc*, 67, 1626 (1945)

[137] Allen, Cadogan, Harris, and Hey, *Chem & Ind (London)*, 1961, 830

[138] Nikushin, Ogibin, Petrov, *Izv Akad Nauk SSSR, Otd Khim Nauk*, 1961, 1326 [C A , 56, 1338 (1962)]

[139] Ladd, U S pat 2,577,422 [C A , 46, 6148 (1952)]

[140] Nikushin, Ogibin, and Petrov, *Tr po Khim i Khim Technol*, 4, 123 (1961) [C A , 55, 27052 (1961)]

[141] Nikushin, Ogibin, and Petrov, *Doklady Akad Nauk SSSR*, 138, 393 (1961) [C A , 55, 22120 (1961)]

[142] Hanford, U S pat 2,433,844 [C A , 42, 2266 (1948)]

[143] C H McDonnel, Ph D Thesis, University of Chicago, 1955

[144] Patrick, U S pat 2,628,238 [C A , 48, 711 (1954)]

[145] Nagasaka, Nukina, and Oda, *J Chem Soc Japan, Ind Chem Sect*, 58, 46 (1955) [C A , 50, 4903 (1956)]

[146] Nagasaka, Nukina, and Oda, *J Chem Soc Japan, Bull Inst Chem Research, Kyoto Univ*, 33, 85 (1955) [C A , 50, 7083 (1956)]

[147] Patrick, U S pat 2,716,684 [C A , 49, 16523 (1955)]

[148] Shuikin and Lebedev, *Doklady Akad Nauk SSSR*, 139, 131 (1961) [C A , 56, 1417 (1962)]

[149] Wallace and Gritter, *J Org Chem*, 26, 5256 (1961)

[150] Lucchesi and Bartok, *J Am Chem Soc*, 82, 4108 (1960)

[151] Bartok and Lucchesi, *J Am Chem Soc*, 81, 5918 (1959)

[152] Ridgway, *Ind Eng Chem*, 50, 1531 (1958)

[153] Lucchesi and Heath, *J Am Chem Soc*, 81, 4770 (1959)

[154] Fuller and Rust, *J Am Chem Soc*, 80, 6148 (1958)

[155] Nikushin, Vorob'ev, and Petrov, *Doklady Akad Nauk SSSR*, 130, 1256 (1960) [C A , 54, 12020 (1960)]

[156] Isaekokov and Mel nikov, *Zhur. Obsch. Khim*, 29, 1233 (1959) [C A , 54, 8599 (1960)]

[157] Ladd, U S pat 2,615,915 [C A , 48, 1416 (1954)]

[158] Vilkas, Dupont, and Dulou, *Bull Soc Chim France*, 1955, 799

[159] Kharasch, Kuderna, and Nudenberg, *J. Org Chem*, 18, 1225 (1953).

# CHAPTER 4

# FORMATION OF CARBON-HETERO ATOM BONDS BY FREE RADICAL CHAIN ADDITIONS TO CARBON-CARBON MULTIPLE BONDS

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## CONTENTS

## INTRODUCTION

Free radical chain addition to carbon-carbon multiple bonds to form carbon-hetero atom bonds is an important synthetic method of wide scope.  Carbon-halogen, carbon-sulfur, carbon-silicon, carbon-germanium, carbon-phosphorus, and carbon-nitrogen bonds have been formed by this method.  In this chapter, the mechanism, scope, limitations, and experimental conditions are treated for the addition reactions that lead to the

formation of the six types of carbon-hetero atom bonds mentioned above *
However, since the direction of addition of free radicals to carbon-carbon
multiple bonds is common to all the classes reviewed, it is taken up briefly
first

In general, experimental procedures for carrying out free radical
additions are similar irrespective of the addendum, hence, we have
chosen to collect representative experimental procedures at the end of the
discussion rather than to include them with the discussions of the classes
to which they belong

A theoretical treatment of free radical addition reactions, generally,
has been given by Walling and Huyser in Chapter 3 of this volume

## ORIENTATION IN FREE RADICAL ADDITIONS

Historically, the orientation in free radical additions of HX compounds
to unsymmetrically substituted olefins has been termed anti-Markownikoff
or abnormal from the relation of the products to those obtained by ionic
addition. Thus the free radical chain addition of hydrogen bromide to
propylene gives n-propyl bromide, whereas ionic addition gives isopropyl
bromide    Present evidence indicates that the orientation in free radical
additions can be most generally correlated by considering the relative
stabilities of the intermediate radicals that can be formed in the addition
step and assuming that the product derives from the more stable radical.
The prediction of relative radical stabilities is based on the premise that
radicals have the following order of decreasing stability: tertiary >
secondary > primary. For example, in the addition of hydrogen bromide
to propylene, the chain-carrying bromine atom could add to give either
1 or 2 as the intermediate radical. The secondary radical 1 would be the

$$CH_3\dot{C}HCH_2Br \qquad CH_3CHBrCH_2\cdot$$
$$\phantom{xxxxx}1 \phantom{xxxxxxxxxxxxxx} 2$$

more stable in this instance and the product of the reaction would be n-
propyl bromide, as observed.   In their broadest sense, the designations
primary, secondary, and tertiary are determined solely by the number of

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* In addition to these rather extensively studied types, there are scattered reports of the
formation of carbon selenium,[1] carbon-oxygen,[2] and carbon tin[3] bonds by free radical chain
addition processes.
[1] Volger and Arens, *Rec Trav Chim*, **77**, 1170 (1958).
[2] (a) Gray and Williams, *Chem Rev*, **59**, 272 (1959), (b) Allison and Cady, *J. Am. Chem.
Soc*, **81**, 1089 (1959), (c) Russell, *ibid*, **78**, 1035 (1956), (d) Kharasch, Arimoto, and
Nudenberg, *J Org Chem*, **36**, 1556 (1951)
[3] (a) Smolin, *Tetrahedron Letters*, **1961**, 143, (b) Beg and Clark, *Chem. & Ind (London)*,
**1962**, 140, (c) Neumann, *Angew. Chem., Intern. Ed Engl*, **2**, 170 (1963)

atoms or groups other than hydrogen on the carbon atom bearing the odd electron, without reference to the carbon skeleton of the radical. Of course, substituents differ in their stabilizing ability so that two radicals of equal multiplicity may differ widely in stability, and a given primary or secondary radical may actually be more stable than a particular secondary or tertiary one. For example, in additions to $\beta$-methylstyrene the intermediate benzyl radical 3 is stabilized by resonance and thus much preferred to the alternative intermediate 4. Accordingly, the radical, $\cdot$X,

$$C_6H_5\overset{\cdot}{C}HCHXCH_3 \qquad\qquad C_6H_5CHXCHCH_3$$
$$\underset{3}{} \qquad\qquad\qquad\qquad \underset{4}{}$$
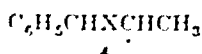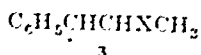
always goes to the $\beta$-carbon atom of the double bond. From studies of radical additions to a group of fluoroölefins the following order of radical stabilizing ability has been derived: $H < F < Cl$.[4] Thus in additions to chlorotrifluoroethylene, radicals attack at $CF_2$ rather than at CFCl to give the intermediate radical 5. In radical additions of hydrogen bromide[5] and methyl mercaptan[6] to trifluoroethylene, both possible adducts are

$$X\cdot + CF_2{=}CFCl \rightarrow XCF_2\overset{\cdot}{C}FCl$$
$$\underset{5}{}$$
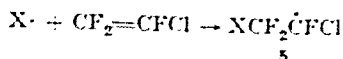
formed, suggesting rather small differences, if any, in the relative stabilities

$$CHF{=}CF_2 + HBr \rightarrow CHFBrCHF_2 + CH_2FCF_2Br$$
$$\underset{(60\%)}{} \qquad\qquad \underset{(40\%)}{}$$
$$CHF{=}CF_2 + CH_3SH \rightarrow CH_3SCHFCHF_2 + CH_3SCF_2CH_2F$$
$$\underset{(75\%)}{} \qquad\qquad \underset{(25\%)}{}$$
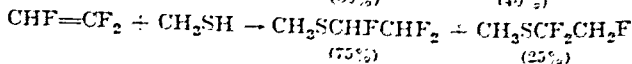
of the intermediate radicals. Other instances are known wherein both possible isomers are formed by the free radical addition. They are discussed in the appropriate sections.

It has been stated[7] that polar and steric factors play little or no part in determining the orientation of radical additions, but recent studies[6] suggest that electronic (polar) factors may play an important role in certain cases, such as those wherein the stabilities of the alternative intermediate radicals do not differ greatly. Be that as it may, the direction of radical attack can generally be predicted by considering only the relative stabilities of the alternative intermediate radicals.

## FREE RADICAL HYDROHALOGENATIONS

The free radical chain addition of hydrogen halides to unsaturates is a convenient and important method for the synthesis of a variety of alkyl

[4] Haszeldine and Steele, J. Chem. Soc., 1957, 2193.
[5] Haszeldine and Steele, J. Chem. Soc., 1957, 2800.
[6] Harris and Stacey, J. Am. Chem. Soc., 83, 840 (1961).
[7] Haszeldine, J. Chem. Soc., 1952, 2561.

and alkenyl halides. Its use as a synthetic procedure is restricted mainly to hydrogen bromide, though a few examples of hydrogen chloride additions are known. The products of the free radical addition are generally isomers of those obtained by the corresponding normal or ionic reaction. Thus propylene gives only isopropyl bromide under ionic conditions, but n-propyl bromide under radical conditions. Exceptions

$$CH_3CH=CH_2 + HBr \begin{array}{c} \xrightarrow{\text{Ionic}} CH_3CHBrCH_3 \\ \\ \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br \end{array}$$
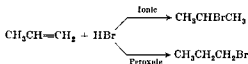
to this rule occur with certain internal olefins where a 50 50 mixture of isomers is frequently formed by either ionic or radical addition, and with $\alpha,\beta$-unsaturated carbonyl compounds where the same product is generally obtained under all conditions. Radical chain additions have not been unequivocally established with the latter compounds, although they probably occur.

This discussion and accompanying tables are concerned with reactions the radical nature of which has been established or is highly probable. Omitted for the most part are those instances where the same product or mixture of products results irrespective of the conditions used. An excellent discussion of the historical aspects of the peroxide effect and of the published results on hydrohalogenation up to 1940 is contained in a review article by Mayo and Walling.[8]

## Mechanism

The most satisfactory mechanism for the abnormal or anti-Markownikoff addition of hydrogen bromide to olefins is the free radical chain process involving bromine atoms as the chain-carrying species first proposed by Kharasch and co-workers[9] and by Hey and Waters.[10]

The steps in the chain propagation are shown. The reaction has

$$Br\cdot + CH_2=CHR \rightarrow BrCH_2\dot{C}HR$$

$$BrCH_2\dot{C}HR + HBr \rightarrow BrCH_2CH_2R + Br\cdot$$
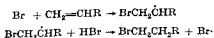
not been investigated from a kinetic viewpoint, but it shows all the usual characteristics associated with radical chain processes. It is initiated by

[8] Mayo and Walling, *Chem Rev*, **27**, 351 (1940).

[9] Kharasch, Engelmann, and Mayo, *J. Org Chem*, **2**, 288 (1937).

[10] Hey and Waters, *Chem Rev*, **21**, 169 (1937).

light,[11] by peroxides,[12] and by other radical generating systems;[13,14] it is inhibited by antioxidants such as hydroquinone and diphenylamine, and it is relatively independent of the polar nature of the solvent.

Initiation of the reaction by peroxides or other radical-producing initiators probably occurs through attack of the initiating radicals (R'·) on hydrogen bromide. However, primary attack of initiator radicals on

$$R'· + HBr \rightarrow Br· + R'H$$
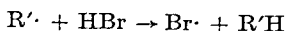
the olefin, followed by transfer with hydrogen bromide cannot be ruled out. Initiation by ultraviolet irradiation in the absence of photosensi-

$$R'· + CH_2{=}CHR \rightarrow R'CH_2\dot{C}HR$$

$$R'CH_2\dot{C}HR + HBr \rightarrow R'CH_2CH_2R + Br·$$
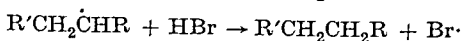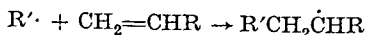
tizers occurs only in the region below about 2900 Å, where hydrogen bromide absorbs. Under these conditions the initiation step must be a homolytic cleavage of the hydrogen bromide.[11]

Freshly reduced iron, nickel, and cobalt have been shown to catalyze the additions to allyl bromide[15,16] and to undecenoic acid.[17,18] It seems probable that their effectiveness as initiators is associated with an ability to generate bromine atoms from hydrogen bromide.[19] Molecular oxygen apparently behaves as an initiator, per se, and not necessarily through the intermediacy of peroxidation of the olefin.[19–21]

Chain termination can occur by any of the following processes.

$$2Br· \rightarrow Br_2$$

$$Br· + BrCH_2\dot{C}HR \rightarrow BrCH_2CH(Br)R$$

$$2BrCH_2\dot{C}HR \rightarrow BrCH_2CH(R)CH(R)CH_2Br$$
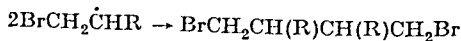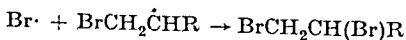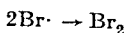
In general, the chains are long, and detectable amounts of the chain-termination products are seldom found. With the single exception of

[11] Vaughan, Rust, and Evans, *J. Org. Chem.*, **7**, 477 (1942).

[12] Kharasch and Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

[13] Rust and Vaughan, U.S. pat. 2,299,411 [*C.A.*, **37**, 1722 (1943)].

[14] Bataafsche Pet. Maatschappij, Brit. pat. 668,159 [*C.A.*, **46**, 7914 (1952)].

[15] Kharasch and Potts, *J. Org. Chem.*, **2**, 195 (1937).

[16] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **12**, 51 (1937); **13**, 400 (1938) [*C.A.*, **31**, 3867 (1937); **32**, 7014 (1938)].

[17] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **13**, 331, 404, 574 (1938) [*C.A.*, **32**, 4944, 7015 (1938); **33**, 132 (1939)].

[18] Takebayashi, *Bull. Chem. Soc. Japan*, **15**, 113, 116 (1940) [*C.A.*, **34**, 5824 (1940)].

[19] Urushibara, *J. Chem. Soc. Japan*, **60**, 717 (1939) [*C.A.*, **36**, 6135 (1942)].

[20] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **11**, 798 (1936); **12**, 138 (1937) [*C.A.*, **31**, 2164, 4641 (1937)].

[21] Urushibara and Simamura, *Bull. Chem. Soc. Japan*, **14**, 323 (1939) [*C.A.*, **34**, 367 (1940)].

vinylidene chloride, which is said to give a 2 1 adduct,[22] there is no report of the formation of telomers of the type $Br(CH_2CHR)_nH$ ($n > 1$)    This fact attests to the great efficiency of hydrogen bromide as a transfer agent

Recently attention has been directed to the steric aspects of free radical additions of hydrogen bromide to olefins and acetylenes    Stereospecific *trans* additions have been noted with both cyclic and acyclic olefins under appropriate conditions    Thus the additions of deuterium bromide to *cis*- and *trans*-2-butene at $-60°$ to $-78°$ give essentially pure ($<1\%$ isomer intercontamination) *threo*- and *erythro*-3-deutero-2-bromobutane, respectively[23]    Additions of hydrogen bromide and deuterium bromide to *cis*- and *trans*-2-bromo-2-butene are stereospecific at $-80°$ in a large excess of the liquid halide[24]    The stereoselectivity decreases with decreasing hydrogen bromide/olefin ratio and with increasing reaction temperature so that at $25°$ the same mixture of 75% *dl*- and 25% *meso*-2,3-dibromobutane is obtained from either *cis*- or *trans*-2-bromo-2-butene    Both *cis*- and *trans*-2-chloro-2-butene are rapidly equilibrated by hydrogen bromide to a mixture containing 80% *trans* and 20% *cis*, even at $-78°$    From either pure *cis*- or pure *trans*-olefin, the adduct consists of a mixture of 70% *threo*- and 30% *erythro*-2-bromo-3-chlorobutane.[25]    Comparison of the product composition with that of the equilibrium mixture of olefin isomers (equilibration having occurred prior to addition) shows that *trans* addition predominates    These additions have been also

Additions to 1-chloro-, 1-bromo-, and 1-methyl-cyclohexene occur with high stereoselectivity to yield *cis*-1-bromo-2-chlorocyclohexane, *cis*-1,2-dibromocyclohexane, and *cis*-1-bromo-2-methylcyclohexane, respectively.[26,27]    Less than 1% of the *trans* isomer is formed with 1-bromocyclohexene.    However, in comparable additions to 1-bromocyclobutene, 1-bromocyclopentene, and 1-bromocycloheptene, the degree of stereoselectivity is lower    The ratios of *cis*:*trans* adducts in these cases are 79.21, 94:6, and 91 9, respectively.[28]    The difference in stereoselectivity with ring size has been attributed to a balance between the mechanistic preference for *trans* addition and the degree of steric inhibition to formation of the *cis* adducts[28]    An interesting case is the hydrobromination of 2-bromo-2-norbornene from which the principal products are *trans* 2,3-dibromomonobornane (6) and *exo cis*-2,3-dibromomonobornane (7), in a ratio

[22] Francis and Leitch, *Can. J. Chem*, 35, 500, (1957)

[23] Skell and Allen, *J Am Chem Soc*, 81, 5383 (1959)

[24] Goering and Larsen, *J Am Chem Soc*, 81, 5937 (1959)

[25] Neureiter and Bordwell, *J Am Chem Soc*, 82, 5354 (1960)

[26] Goering, Abell, and Aycock, *J Am Chem Soc*, 74, 3588 (1952)

[27] Goering and Sims, *J Am Chem Soc*, 77, 3465 (1955)

[28] Abell and Chiao, *J Am Chem Soc*, 82, 3610 (1960).

of about 5:2.[29]   The formation of both of these products can be explained
by an initial *exo* attack of a bromine atom followed by transfer with
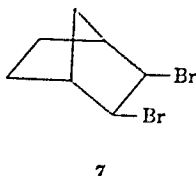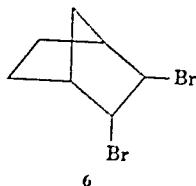


hydrogen bromide.   The major product derives from transfer from the
less sterically hindered *exo* side and is formally then a *cis* addition.
Adduct 7, on the other hand, derives from the usually dominant *trans*
addition, inhibited in the present case by the steric factor.

Both *cis* and *trans* additions to acetylenes have been reported.   Propyne
gives solely *cis*-1-bromo-1-propene when irradiated in the liquid phase at
−60° to −78°.[30]   In the gas phase, rapid equilibration of the product
prevented determination of the degree of stereoselectivity.   The formation
of *dl*-2,3-dibromobutane by addition of hydrogen bromide to 2-butyne[31]
almost certainly involves two consecutive stereospecific *trans* additions,
although this was not recognized at the time the work was done.   Addi-
tions to 1-bromopropyne and to 1-bromo-3,3-dimethyl-1-butyne have been
reported to yield predominantly *trans*-1,2-dibromopropene and *trans*-1,2-
dibromo-3,3-dimethyl-1-butene, respectively, by *cis* additions.[32]   The
addition of hydrogen bromide to phenylpropiolic acid in benzene solution
forms *trans*-α-bromocinnamic acid in 95% yield.[33]   The radical nature of
this addition, although not proved, seems probable in view of the fact that
catechol inhibits the formation of this product.   Further studies appear
to be required to elucidate the apparent differences in the stereochemistry
of the additions to acetylenes.

The high degree of stereoselectivity observed in hydrogen bromide
additions requires that the rate of the chain transfer step compete success-
fully with that of radical interconversion through rotation about a C—C
bond or, in the case of cyclic compounds, with conformational isomeriza-
tion.   Several proposals have been put forward to rationalize the stereo-
selectivity and dominant *trans* addition.   An intermediate with the
bridged structure 8, together with contributing forms containing three-
electron bonds, has been considered.[26]   The possibility of existence of

[29] LeBel, *J. Am. Chem. Soc.*, 82, 623 (1960).
[30] Skell and Allen, *J. Am. Chem. Soc.*, 80, 5997 (1958).
[31] Walling, Kharasch, and Mayo, *J. Am. Chem. Soc.*, 61, 1711 (1939).
[32] L. D. Bergel'son, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1960, 1145.
[32] Kasiwagi, *Bull. Chem. Soc. Japan*, 25, 81 (1952); 31, 985 (1958).

such an intermediate at low temperatures has been demonstrated by EPR studies.[34] However, the concept appears inadequate to explain some of the observations in hydrogen bromide additions [23]

$$\underset{\underset{\mathbf{8}}{\overset{|}{\underset{Br}{}}}}{-C}\overline{\quad\quad}\overset{|}{C-}$$

An alternative proposal envisions reaction between a bromine atom and an olefin hydrogen bromide complex[21,27,30] as a means of rapid hydrogen atom transfer  Neureiter and Bordwell[25] have recently proposed a polar-steric scheme wherein the development in the transition state 9 of a dipole,

$$\underset{\mathbf{9}}{\overset{\delta+}{\underset{}{}}{-C}\overset{\diagdown}{\quad}\quad H \quad X^{\delta-}}$$
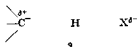
oriented away from the largest permanent (negative) dipole on the saturated carbon atom, causes the molecule undergoing transfer to approach the radical center *trans* to the most negative group on the saturated carbon atom

## Scope and Limitations

The radical addition of hydrogen bromide has been applied to a considerable variety of unsaturated compounds, *including terminal olefins*, halogenated ethylenes, internal (including cyclic) olefins, mono- and disubstituted acetylenes, vinylsilanes, etc. The reaction with terminal olefins is a very general one for the synthesis of the corresponding 1-bromoalkanes, although substitution of certain groups such as chlorine, bromine, or carboxyl on the terminal carbon atom of the double bond can direct the addition to yield the 2-bromo adduct as in the following examples [9]

$$CH_3CH{=}CHCl + HBr \xrightarrow{(C_6H_5COO)_2} CH_3CHBrCH_2Cl$$

$$CH_3CH{=}CHBr + HBr \xrightarrow{(C_6H_5COO)_2} CH_3CHBrCH_2Br$$
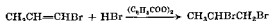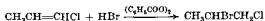
1-Bromo-1-hexene, which reacts only very slowly with hydrogen bromide in the presence of an antioxidant, gives a 75% yield of 1,2-dibromohexane in 1 5 hours at 10° in the presence of a trace of peroxide.[35]

[34] Abell and Piette, *J. Am Chem Soc*, **84**, 916 (1962)

[35] Young, Vogt, and Nieuwland, *J. Am. Chem Soc*, **58**, 1806 (1936)

The direction of addition to allylsilanes is remarkable in that some reactions lead to Markownikoff products even in the presence of peroxides.[36,37]

$$ClSi(CH_3)_2CH_2CH{=}CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} ClSi(CH_3)_2CH_2CHBrCH_3$$

$$(CH_3)_3SiCH_2CH{=}CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} (CH_3)_3SiCH_2CHBrCH_3$$

However,

$$Cl_3SiCH_2CH{=}CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} Cl_3SiCH_2CH_2CH_2Br$$
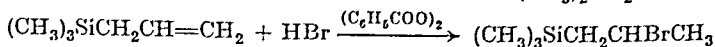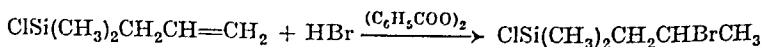
$$Cl_2Si(CH_3)CH_2CH{=}CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} Cl_2Si(CH_3)CH_2CH_2CH_2Br$$
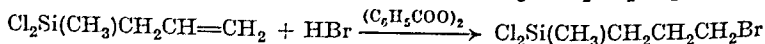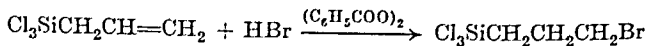
These observations might be considered manifestations of the predominance of ionic addition in certain reactions and of radical addition in others, but this seems unlikely in view of the fact that yields are high and mixtures of isomers are apparently not obtained.

Unequivocal evidence for radical chain addition to $\alpha,\beta$-unsaturated acids and esters has not been presented, and it is reported in nearly all cases studied that the same products (the $\beta$-bromo acids or esters) are obtained in the presence or absence of peroxides or antioxidants.* This may mean that the ionic addition predominates under all conditions, but it is more likely that it merely indicates the operation of a directive influence of the terminal carboxyl or carbalkoxyl group in the radical addition process. As with terminal olefins, so also with monosubstituted acetylenes the 1:1 products are those deriving from attachment of the bromine atom to the terminal carbon atom.[30,35,39,40] In the presence of excess hydrogen bromide, the alkenyl halides react further to give, in all cases, the 1,2-dibromoalkanes.[30,35,41]

The orientation in additions of hydrogen bromide is generally that which would be predicted on the basis of intermediate radical stabilities. Thus propylene gives only $n$-propyl bromide and 1-chlorocyclohexene gives only 1-chloro-2-bromocyclohexane. However, the orientation with some fluoroölefins, is less clear cut. For example, 1,1-difluoropropene is reported to yield 2-bromo-1,1-difluoropropane;[42] and trifluoroethylene gives a mixture of the two possible isomers, 1-bromo-1,2,2-trifluoro- and

[26] Sommer, Tyler, and Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

[37] Mironov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1959, 1781.

* The apparent lone exception is the addition to phenylpropiolic acid, where the product in non-polar solvents under oxidant conditions is $\alpha$-bromocinnamic acid.[23] The orientation of adduct in this case is that expected for radical addition, considering intermediate radical stabilities. The $\beta$-bromo adduct is obtained in polar solvents.[28]

[38] Michael, *J. Org. Chem.*, **4**, 128 (1939).

[39] Haszeldine, *J. Chem. Soc.*, 1952, 3490.

[40] Harris and Smith, *J. Chem. Soc.*, 1935, 1572.

[41] Kharasch, McNab, and McNab, *J. Am. Chem. Soc.*, **57**, 2463 (1935).

[42] Haszeldine, *J. Chem. Soc.*, 1953, 3565.

1-bromo-1,1,2-trifluoro-ethane in a ratio of about 60:40, both formed by the radical chain mechanism.[43] Similarly, hexafluoropropene yields both possible isomers in the ultraviolet- or x-ray-induced reaction.[44]

Free radical chain additions of hydrogen fluoride or of hydrogen iodide to olefins have never been observed. The energetics of the chain propagation steps for the addition of the various hydrogen halides to ethylene are shown in Table I [45]

The failure of hydrogen fluoride to add is undoubtedly due to the very high strength of the hydrogen-fluorine bond. The energetics for radical

TABLE I

| H—X | $\Delta H$ (kcal./mole at 25°)<br>X· + $CH_2$=$CH_2$ | $\Delta H$ (kcal./mole at 25°)<br>$XCH_2CH_2$· + H—X |
|---|---|---|
| H—F | — | 37 |
| H—Cl | −26 | 5 |
| H—Br | −5 | −11 |
| H—I | 7 | −27 |

addition of hydrogen iodide indicate that attack of the iodine atom on the double bond should be slow. Another difficulty with the addition of hydrogen iodide is the catalysis of the ordinarily rapid ionic addition by iodine. Very few radical additions of hydrogen chloride to olefins have been demonstrated. Addition to ethylene has been observed to occur in the vapor phase under the influence of either ultraviolet radiation or radicals generated from di-t-butyl peroxide.[46] Only a very slow addition to propylene was observed under these conditions, and isobutylene proved to be an inhibitor for the ethylene addition. In the liquid phase, additions to t-butylethylene,[47] allyl chloride,[48] and propylene[48] have been reported, but in all cases the chain lengths are short and the major products obtained are those resulting from the competing ionic additions. Low telomers are also generally found, and, in fact, a whole series of even-numbered n-alkyl chlorides has been obtained by heating ethylene at high pressure (100–1000 atm.) with aqueous hydrochloric acid at 100° in the presence of benzoyl peroxide [49] In general, the radical chain addition of hydrogen chloride to olefins is not a useful preparative method.

43 Haszeldine and Steele, J. Chem. Soc., 1957, 2800
44 Stacey and Harris, J. Org. Chem., 27, 4089 (1962)
45 Walling, Free Radicals in Solution, John Wiley and Sons, Inc, New York, 1957.
46 Raley, Rust, and Vaughan, J. Am. Chem. Soc., 70, 2767 (1948)
47 Ecke, Cook, and Whitmore, J. Am. Chem. Soc., 72, 1511 (1950).
48 Mayo, J. Am. Chem. Soc., 76, 5392 (1954)
49 Ford, Hanford, Harmon, and Lipscomb, J. Am. Chem. Soc., 74, 4323 (1952).

Examples of radical rearrangement in hydrogen bromide additions have been reported by Nesmeyanov and his co-workers.[50-53]  The rearrangements all involve a 1,2 shift of a chlorine atom, as illustrated in the accompanying equation.  The major product of addition to 3,3,3-trichloropropene is, accordingly, not 1,1,1-trichloro-3-bromopropane as

$$Cl_3CCH{=}CH_2 + Br\cdot \longrightarrow Cl_3C\overset{\cdot}{C}HCH_2Br$$

$$Cl_2CHCHClCH_2Br + Br\cdot \xleftarrow{\ HBr\ } Cl_2\overset{\cdot}{C}CHClCH_2Br$$
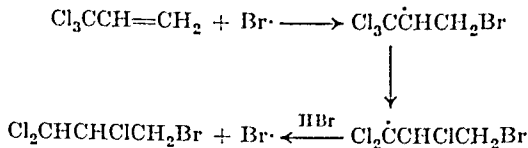
originally thought,[51] but 1,1,2-trichloro-3-bromopropane.[50]  Similarly, the olefins 3,3,3-trichloro-2-methylpropene, 2,3,3,3-tetrachloropropene, and 3,3-dichloro-1-butene add hydrogen bromide in the presence of peroxide to give the rearranged adducts 1-bromo-2,3,3-trichloro-2-methylpropane,[51] 1-bromo-2,2,3,3-tetrachloropropane,[52] and 1-bromo-2,3-dichlorobutane,[55] respectively, as the major products.  By contrast, 2,3,3-trichloropropene gives the unrearranged adduct, 1-bromo-2,3,3-trichloropropane,[52] while 3,3-dichloro-2-methylpropene,[55] 3,3-dichloropropene,[55,56] and 3-fluoro-3,3-dichloropropene[57] give mixtures of rearranged and unrearranged adducts.

## Experimental Conditions

An important consideration in any attempt to prepare specific halides by the free radical addition of hydrogen bromide (or hydrogen chloride) to unsaturates is the relative rates of the competing ionic and radical additions.  The rates of the uncatalyzed ionic addition vary markedly from one olefin to another.  Consequently, the precautions required to avoid interference by the ionic addition vary widely.  When the ionic addition is extremely slow, as with such olefins as 1-bromopropene[9] or

[50] Nesmeyanov, Freidlina, and Zakharkin, *Doklady Akad. Nauk SSSR*, **81**, 199 (1951) [*C.A.*, **47**, 3789 (1953)].

[51] Nesmeyanov, Freidlina et al., *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1959, 992.

[52] Freidlina, Kost, Khorlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **128**, 755 (1959).

[53] Nesmeyanov, Freidlina, Kost, and Khorlina, *Tetrahedron*, **16**, 94 (1961).

[54] Kharasch, Rossin, and Fields, *J. Am. Chem. Soc.*, **63**, 2558 (1941).

[55] Freidlina, Kost, Khorlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **137**, 292 (1961).

[56] Freidlina, Khorlina, and Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1960, 622.

[57] Kost, Sidorova, Freidlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **132**, 569 (1960).

trichloroethylene,[58] the radical addition predominates under all conditions except those in which radical initiation is excluded most rigorously    At the other extreme are compounds such as styrene and trimethylethylene which react so rapidly by the ionic mechanism that it is necessary to use high dilution techniques to obtain the products of radical addition    For the great majority of olefins which fall between these extremes, it is a fairly simple matter to effect predominantly ionic or radical addition by the use of free radical inhibitors (e g , hydroquinone, diphenylamine, or thiophenol) or initiators (e g , peroxides, ultraviolet light, etc ), respectively

Aside from the necessity of avoiding ionic reaction, the choice of conditions for carrying out the free radical addition can be a rather arbitrary matter    The reaction can be run in the presence or absence of a solvent and over a temperature range from $-80°$ or lower to $+100°$ or higher with appropriate initiators    A wide variety of substances are effective as initiators    By far the most commonly used substances are peroxides especially acyl peroxides such as benzoyl peroxide    In early work, the naturally occurring endo peroxide, ascaridole, was widely used, but it has now been largely superseded by other peroxides    The reaction can also be initiated photochemically with ultraviolet radiation of wavelength below about 2900 Å or with light of longer wavelength in combination with photosensitizers such as carbonyl compounds[59] or metal alkyls.[60] Ultraviolet initiation is especially convenient for low-temperature reactions, e g , with low-boiling olefins or where stereospecificity of addition is sought    α-Haloketones initiate the reaction even in the dark,[13] and finely divided metals such as iron, cobalt, and nickel are reported to be effective initiators [16,61] Silent electrical discharges have been used to initiate the reaction in the vapor phase,[11] but this does not suggest itself as a generally convenient preparative procedure.

The effect of solvents on the addition of hydrogen bromide to unsaturates was the subject of prolonged debate in the early studies of peroxide effects. The situation now appears to be fairly clear in view of the recognition of a competition between ionic and radical additions in most systems    The radical addition is fairly insensitive to solvent polarity, but this is not true of the ionic addition    Accordingly, the use of a non-polar solvent (e g , pentane), which diminishes the rate of ionic addition, is favorable to the formation of the radical addition product    In fact, such reactive (ionically) olefins as styrene and trimethylethylene require high dilution in

[58] Kharasch, Norton, and Mayo, J Org Chem , 3, 48 (1938)

[59] Vaughan and Rust, U S pat 2,398,481 [C A , 40, 3764 (1946)].

[60] Evans, Vaughan, and Rust, Brit pat 567,524, U S pat 2,376,675 [C A , 39, 3533 (1945)]

[61] Urushibara and Takebayashi, Bull Chem Soc Japan, 11, 692, 754 (1936) [C A , 31, 1757, 1758 (1937)]

non-polar media for successful radical addition. Radical addition is easily obtained in many solvents—an indication that their inhibiting properties are usually negligible. With solvents containing labile hydrogen atoms (i.e., readily transferable in radical reactions), inhibition does occur and the effect appears to increase with increasing temperature. In the presence of peroxides, no radical addition to trimethylethylene occurs above 20° in ethanol or above 0° in methanol.[62] The ultraviolet-catalyzed addition of hydrogen bromide to allyl bromide proceeds well in heptane, carbon disulfide, acetyl bromide, or benzoyl chloride, but in acetic acid only traces of 1,3-dibromopropane are obtained.[8] Goering and Sims[27] have reported that the radical additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene can be promoted by ultraviolet light in pure pentane, in a mixture of 31 mole % diethyl ether in pentane, or in a homogeneous equimolar mixture of hydrogen chloride and pentane. However, in anhydrous ether, the reaction could not be so induced and the sole product was the 1,1-dihalide resulting from ionic addition.

The radical addition reaction appears to have a greater temperature coefficient than the ionic addition for all those hydrogen bromide-olefin combinations which have been studied. As a result, higher temperatures favor predominance of the radical reaction. For example, air does not initiate much addition of hydrogen bromide to allyl bromide at 0°, but it does at room temperature.[12] Similarly, in the addition to 1-methylcyclohexene, the ionic addition product is formed exclusively at −80°, but at 0° it constitutes only 64% and at 65° only 22% of the total adduct.[26] Nevertheless, it is often possible to effect radical additions to the complete exclusion of ionic reaction even at temperatures as low as −80°. This can be of considerable significance in stereospecific additions wherein the thermodynamically less stable isomer is sometimes formed.

## RADICAL ADDITIONS TO CARBON-CARBON UNSATURATES TO FORM SULFUR-CARBON BONDS

Several species of sulfur compounds, e.g., thiols, hydrogen sulfide, bisulfite ion, sulfenyl halides, sulfur chloride pentafluoride, sulfonyl and sulfuryl halides, add by radical mechanisms to olefinic and acetylenic compounds to form carbon-sulfur bonds. Each of these classes constitutes a relatively large subject and will be considered separately. The radical copolymerization of sulfur dioxide with olefins* also involves the formation of carbon-sulfur bonds, but, since it is of rather specialized interest, it has not been included in this chapter.

[62] Michael and Weiner, *J. Org. Chem.*, **4**, 531 (1939).
* Olefin-sulfur dioxide copolymerizations have been reviewed by Walling in ref. 45, p. 223.

## Addition of Thiols to Olefins and Acetylenes

Thiols add to olefins and acetylenes via a free radical chain mechanism to form sulfides. The reaction is characteristic of thiols generally, e g., hydrogen sulfide (p 191), alkanethiols, aromatic and heterocyclic thiols,

$$RSH + C=C \rightarrow RSC-CH$$
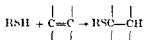
thiolcarboxylic acids, and thiolphosphoric acids. The usual free radical initiators, such as oxygen, peroxides, azonitriles, and ultraviolet radiation, are effective in initiating the reaction.

Apparently the first recorded example of the reaction was the anti-Markownikoff addition of thiophenol to styrene reported by Posner in 1905.[63] Ashworth and Burkhardt, repeating Posner's experiments in

$$C_6H_5SH + C_6H_5CH=CH_2 \rightarrow C_6H_5SCH_2CH_2C_6H_5$$
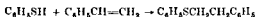
1928, noted that exposure to sunlight produced a significant acceleration in the rate of addition and that piperidine retarded it.[64] Subsequently Burkhardt postulated the phenylthiyl radical ($C_6H_5S\cdot$) as an intermediate in the reaction.[65] The catalytic influence of peroxides was reported in 1938 by Kharasch, Read, and Mayo[66] and by Jones and Reid.[67] The currently accepted radical chain mechanism was formulated by Kharasch, Read, and Mayo in that year.[66]

Addition of thiols to unsaturates can also occur by ionic mechanisms. Examples are acid-[66] or sulfur-[67]catalyzed addition to olefins and acetylenes and base-catalyzed addition to α,β-unsaturated carbonyl compounds

$$C_6H_5SH + CH_2=C(CH_3)_2 \xrightarrow{Acid} C_6H_5SC(CH_3)_3$$
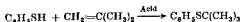
pounds and nitriles.[69] These ionic additions generally give products

$$C_6H_5SH + CH_2=CHCN \xrightarrow{Base} C_6H_5SCH_2CH_2CN$$
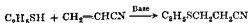
resulting from normal (Markownikoff) addition, whereas characteristically abnormal Jones and Reid[67] were the first to demonstrate that either normal or abnormal 1 : 1 adducts can be obtained from addition of a thiol to an olefin, depending upon the catalyst used

[63] Posner, Ber, 38, 646 (1905)

[64] Ashworth and Burkhardt, J Chem Soc, 1928, 1791

[65] Burkhardt, Trans Faraday Soc, 30, 18 (1934).

[66] Kharasch, Read, and Mayo, Chem & Ind (London), 57, 752 (1938)

[67] Jones and Reid, J Am Chem Soc, 60, 2452 (1938)

[68] Ipatieff, Pines, and Friedman, J Am Chem Soc, 60, 2731 (1938)

[69] Kharasch and Fuchs, J Org Chem, 13, 97 (1948).

$$C_2H_5SH + CH_2\!\!=\!\!CHC_6H_{13}\text{-}n \quad \overset{\text{Sulfur}}{\underset{180°}{\nearrow}} \quad C_2H_5SCH(CH_3)C_6H_{13}\text{-}n$$

$$\overset{\text{Peroxide}}{\underset{180°}{\searrow}} \quad C_2H_5SCH_2CH_2C_6H_{13}\text{-}n$$
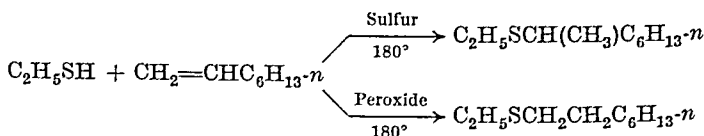
Radical and ionic additions to $\alpha,\beta$-unsaturated carbonyl compounds and nitriles lead to the same product. Reviews of the additions of thiols to olefins have been made by Mayo and Walling,[8] Walling (ref. 45, pp. 313 ff.), and Knunyants and Fokin.[70]

**Mechanism.** Studies of the mechanism of radical thiol additions have dealt largely with additions to olefins. Acetylene additions have apparently not been studied in this respect. The reaction is generally considered to proceed via a multistep chain mechanism.[66,71] The chain

Initiation:                                $RSH \rightarrow RS\cdot$

Addition:        $RS\cdot + \underset{|}{\overset{|}{C}}\!\!=\!\!\underset{|}{\overset{|}{C}} \rightarrow RS\!-\!\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot$

Chain transfer:   $RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot + RSH \rightarrow RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}H + RS\cdot$

Propagation:   $RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot + \underset{|}{\overset{|}{C}}\!\!=\!\!\underset{|}{\overset{|}{C}} \rightarrow RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot$

Termination:
$$2RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot \rightarrow RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}SR$$

$$2RS\cdot \rightarrow RSSR$$

$$RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}\cdot + RS\cdot \rightarrow RS\underset{|}{\overset{|}{C}}\!-\!\underset{|}{\overset{|}{C}}SR$$
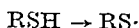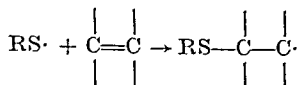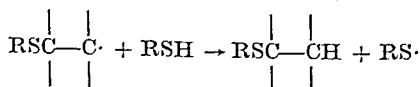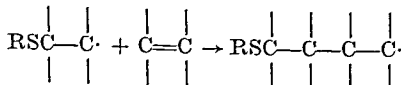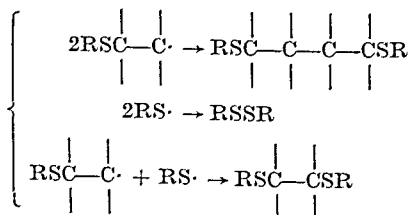
nature of the reaction is indicated by the acceleration produced by ultraviolet radiation and by the observation that, in reactions initiated by free radical initiators, only minute amounts of these materials are required. Kinetic chain lengths of $10^4$ have been reported.[71] Each step in the mechanism shown will be discussed in some detail in the following paragraphs.

*Initiation.* Generation of a thiyl radical from a thiol can be accomplished by means of the decomposition of a peroxide, an azonitrile, or other radical-generating species in the reaction mixture, by irradiation

[70] Knunyants and Fokin, *Usp. Khim.*, **19**, 545 (1950).
[71] Back, Trick, McDonald, and Sivertz, *Can. J. Chem.*, **32**, 1078 (1954).

of the thiol with x-rays,[6 72] $\gamma$-rays,[72 73] or $\beta$-rays,[74] or by direct photolysis of the thiol with ultraviolet radiation  The mechanism of initiation with radical-producing agents consists of abstraction of hydrogen from a thiol molecule by a radical produced in the reaction mixture, thus a thiyl

$$X + RSH \rightarrow RS + HX$$

radical is generated.   When ultraviolet radiation capable of thiol photolysis is employed, both a thiyl radical and a hydrogen atom are produced.[75] Likely fates for the hydrogen atom are (a) addition to the olefin ultimately

$$RSH \rightarrow RS + H$$

producing a thiyl radical and a molecule of alkane, and (b) attack on the thiol to produce molecular hydrogen and a thiyl radical.

$$H + CH_2=CHR \rightarrow CH_3\dot{C}HR$$

$$CH_3\dot{C}HR + RSH \rightarrow CH_3CH_2R + RS$$

$$H + RSH \rightarrow H_2 + RS$$
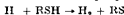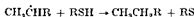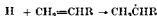
Thus, in ultraviolet initiation, both radical species produced can start kinetic chains   Since the reactions producing the 1:1 adduct are generally of great chain length, the yield of molecular hydrogen and alkane will be small compared to the yield of the olefin-thiol addition product.   However, in the photoinitiated addition of butanethiol to vinyl acetate, both hydrogen and ethyl acetate have been found [76]

*Addition and Chain Transfer*   In a typical thiol addition, both the addition and the chain transfer are quite exothermic, and thus, once the thiyl radical is generated, a rapid chain reaction can ensue (ref. 45, pp. 313 ff )

$$CH_3S\cdot + CH_2=CH_2 \rightarrow CH_3SCH_2CH_2 \qquad \Delta H = -14 \text{ kcal /mole}$$

$$CH_3SCH_2CH_2 + CH_3SH \rightarrow CH_3SCH_2CH_3 + CH_3S \qquad \Delta H = -12 \text{ kcal /mole}$$
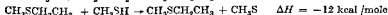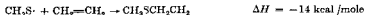
There is ample evidence that in some cases the addition step is reversible.[25,77–80]   On the basis of determination of negative over-all activation energies for gas phase photoinitiated addition of methanethiol to isobutylene, propylene, and ethylene, Sivertz and co-workers concluded

[72] Fontijn and Spinks, *Can J Chem* , 35, 1384, (1957)

[73] Fontijn and Spinks, *Can J Chem* , 35, 1397 (1957).

[74] Chapman, *J Phys Chem* , 64, 1355 (1960)

[75] Inaba and Darwent, *J Phys Chem* , 64, 1431 (1960)

[76] Yamaguchi, Araki, Suzuki, and Hoshino, *Bull Chem. Soc. Japan*, 33, 528 (1960).

[77] Sivertz, Andrews, Elsdon, and Graham, *J. Polymer. Sci* , 19, 587 (1956).

[78] Fallon and Sivertz, *Can J Chem* , 25, 723 (1957).

[79] Sivertz, *J Phys Chem* , 63, 34 (1959).

[80] Walling and Helmreich, *J Am. Chem. Soc* , 81, 1144 (1959).

that the addition step in these reactions is reversible.[77]   Experimentally, the isomerization of pure *cis-* or *trans-*olefins by small amounts of thiol has been given as evidence for reversibility of the addition step.   For example, either *cis-* or *trans-*2-butene is equilibrated by small amounts of methanethiol,[80] indicating that the thiyl radical adds to the olefin to give an intermediate radical which equilibrates and then largely dissociates to the thiyl radical and a mixture of the *cis-* and *trans-*olefin.   At 60°, the reverse reactions are 20 and 85 times as fast as the chain transfer step for the *cis* and *trans* isomers, respectively.[80]
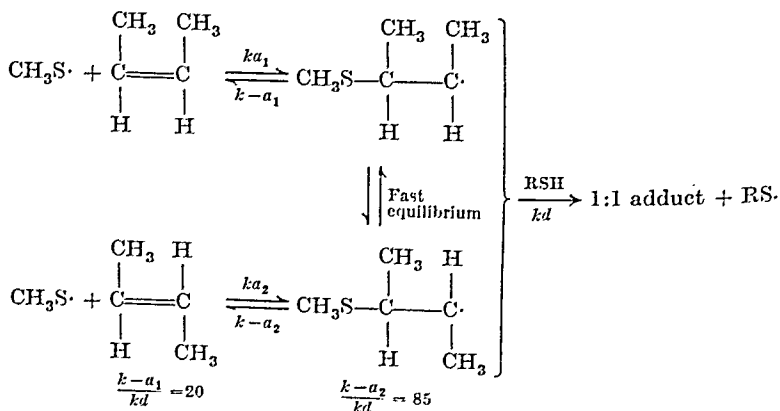


Similarly, *cis-* or *trans-*2-butene is isomerized by small amounts of thiolacetic acid upon ultraviolet irradiation at room temperature, but at −78° no isomerization occurs.[25]   With terminal olefins, and with olefins from which resonance-stabilized intermediate radicals are formed by addition of a thiyl radical (e.g., β-methylstyrene and methyl acrylate), the addition step is considerably less reversible.[80]   The formation of thiol and olefin in the decarbonylation of β-alkylmercaptoaldehydes affords additional evidence of the reversibility of the addition step.[81]

$$RSCH_2CH_2CHO \rightarrow RSCH_2CH_2\overset{\overset{O}{\|}}{C}\cdot \rightarrow RSH + CH_2{=}CH_2 + CO$$
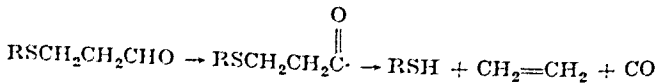
A vast amount of information concerning the relative reactivities of thiols in the chain transfer step has been obtained from the determination of thiol transfer constants in vinyl polymerizations (ref. 45, p. 319). From such studies it has been found that thiols with electron-withdrawing groups (e.g., $CO_2H$, $C_6H_5$) are enhanced in reactivity, whereas those with

[81] Foster, Larchar, Lipscomb, and McKusick, *J. Am. Chem. Soc.*, **78**, 5606 (1956).

electron-donating groups (e g, $t$-butyl and $t$-octyl) are less reactive than primary alkanethiols.

Kinetic studies[71-74 78-80 82] have afforded considerable insight into the effect of structure on reactivity, particularly with respect to the addition and transfer steps. It has been claimed that thiyl radicals are electrophilic in nature, since in a series of competitive experiments involving the addition of mercaptoacetic acid to substituted α-methylstyrenes it was found that electron-donating groups in the $p$-position increase the rate of reaction.[83]

$$X-\!\!\!\!\!\overset{\displaystyle CH_3}{\underset{}{\bigcirc}}\!\!\!\!\!-C\!=\!CH_2 + HSCH_2CO_2H \rightarrow X-\!\!\!\!\!\overset{\displaystyle CH_3}{\underset{}{\bigcirc}}\!\!\!\!\!-CHCH_2SCH_2CO_2H$$

$$(X = CH_3O > CH_3 > H > Br > F)$$
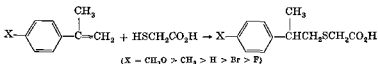
Polar structures 11 and 12 contributing to the transition state have been proposed to account for this effect *
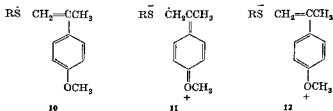


The effects of structure on the rates of both the addition step and the chain transfer step leading to the 1:1 adduct have been studied by Sivertz[71,78,82] and by Walling[80]  Generally, the transfer step is the slower, rate-determining step, being first order in the thiol †  For example, the intermediate radical in the $n$-butanethiol-styrene reaction is a resonance-stabilized radical 13; consequently, the addition step leading to its formation is relatively fast and the transfer step is relatively slow (Table II)[78]

$$n\text{-}C_4H_9S\cdot + CH_2\!=\!CHC_6H_5 \rightarrow n\,C_4H_9SCH_2\dot{C}HC_6H_5 \rightarrow n\text{-}C_4H_9SCH_2CH_2C_6H_5$$
$$13$$

---
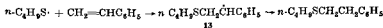
[82] Onyszchuk and Sivertz, Can. J Chem, 33, 1034 (1955)

[83] Walling, Seymour, and Wolfstirn, J. Am Chem. Soc., 70, 2559 (1948)

* Polar structures can also be correlated with the relative stabilities of the intermediate benzyl radicals, i e, the more stable the intermediate benzyl radical, the faster is the rate of its formation. An experiment with $p$ nitro- or $p$-cyano α methylstyrene might help to establish the more electrophilic nature

† If the addition step were the slow step, the rate of the over all reaction would depend on the olefin concentration.

<div align="center">

TABLE II[78,79]

ADDITION, TRANSFER, AND TERMINATION RATES
(LITERS/MOLES SEC.) AT 25°

</div>

|  | $k$ (Addition) | $k$ (Chain Transfer) | $k$ (Termination) |
|---|---|---|---|
| $n$-Butanethiol-styrene | $1.2 \times 10^9$ | $1.24 \times 10^3$ | $5 \times 10^8$ |
| $n$-Butanethiol-1-pentene | $7 \times 10^6$ | $1.4 \times 10^6$ | $6 \times 10^{11}$ |
| Thiophenol-styrene | — | $3 \times 10^3$ | $2 \times 10^7$ |
| $n$-Butanethiol-isoprene | — | 93 | $1.4 \times 10^8$ |

In the addition of $n$-butanethiol to 1-pentene, the addition step is slow

$$n\text{-}C_4H_9S\cdot + CH_2{=}CHC_3H_7\text{-}n \rightarrow n\text{-}C_4H_9SCH_2\dot{C}HC_3H_7\text{-}n \xrightarrow{n\text{-}C_4H_9SH}$$

$$\mathbf{14}$$

$$n\text{-}C_4H_9SCH_2CH_2C_3H_7\text{-}n + n\text{-}C_4H_9S\cdot$$
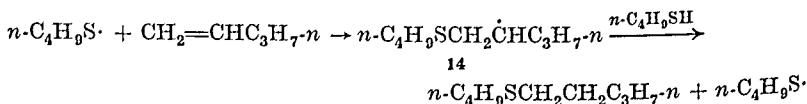
relative to the $n$-butanethiol-styrene reaction since no resonance stabilization is possible in the intermediate radical 14. For the same reason, the transfer step is fast relative to the $n$-butanethiol-styrene reaction (Table II). The rates of the two steps in the $n$-butanethiol-pentene reaction are close enough that the over-all rate of reaction shows some dependence on the olefin concentration, although it is still largely first-order in the thiol. A consequence of the difference between the rates of the addition steps in the $n$-butanethiol-styrene and $n$-butanethiol-pentene additions is that, even though the over-all rate of the $n$-butanethiol-pentene reaction is 20 times that of the $n$-butanethiol-styrene reaction, in a competitive experiment styrene reacts preferentially.

In the addition of thiophenol to styrene the transfer step is again rate-

$$C_6H_5S\cdot + CH_2{=}CHC_6H_5 \rightarrow C_6H_5SCH_2\dot{C}HC_6H_5 \xrightarrow{C_6H_5SH}$$

$$\mathbf{15}$$

$$C_6H_5SCH_2CH_2C_6H_5 + C_6H_5S\cdot$$
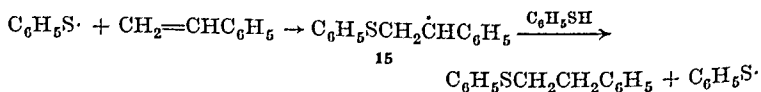
controlling (first-order in thiol) owing to the large resonance stabilization possible in the intermediate radical 15.[78]

In contrast to the preceding systems, the over-all rate of the thiophenol-1-octene reaction is first-order in both thiol and olefin.[78] Although no

$$C_6H_5S\cdot + CH_2{=}CHC_6H_{13}\text{-}n \rightarrow C_6H_5SCH_2\dot{C}HC_6H_{13}\text{-}n \xrightarrow{C_6H_5SH}$$

$$\mathbf{16}$$

$$C_6H_5SCH_2CH_2C_6H_{13}\text{-}n + C_6H_5S\cdot$$
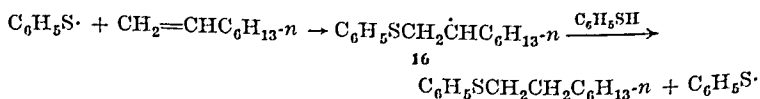
values for the individual rates have been given, it seems that here the addition step is slower than that in the previously discussed cases since it

involves the addition of a resonance-stabilized phenylthiyl radical to form an intermediate radical 16 which is not resonance-stabilized    The transfer step should be relatively fast compared to the previously discussed systems since it results in the formation of the phenylthiyl radical    The over-all rate of the thiophenol-1-octene reaction is less than that of the thiophenol-styrene reaction, presumably because of the slow addition step in the octene reaction [78]

From the discussion above and from a series of competitive experiments of dodecanethiol at 60° with several olefins (Table III),[89] the following

## TABLE III

### RELATIVE REACTIVITIES OF OLEFINS TOWARD DODECANETHIOL AT 60°[89]

| Olefin | Relative Reactivity | Olefin | Relative Reactivity |
|--------|--------------------|--------|--------------------|
| Styrene | 17 | Allylbenzene | 1 0 |
| β-Methylstyrene | 5 5 | Vinyl acetate | 0.8 |
| Vinyl n-butyl ether | 3 9 | Allyl chloride | 0 7 |
| Methyl methacrylate | 2 4 | Cyclopentene | 0 6 |
| Methyl acrylate | 2 0 | Allyl acetate | 0 6 |
| Allyl alcohol | 1.5 | Allyl cyanide | 0 4 |
| 2-Methyl-1-butene | 1.2 | Cyclohexene | 0 3 |
| 1-Octene | 1 0 | cis-Dichloroethylene | <0 2 |

conclusions concerning the effect of olefin structure on the rate of the addition step can be drawn: (a) reactivity is increased if the intermediate radical is resonance-stabilized and, conversely, it is decreased if the thiyl radical is resonance-stabilized; (b) electron-donating groups in the olefin increase the rate, while electron-withdrawing groups decrease the rate; (c) terminal double bonds are more reactive than internal ones; (d) cyclopentene is more reactive than cyclohexene.

*Propagation.*    The importance of propagation leading to telomers depends on the nature of the olefin and on the transfer activity of the thiol. Generally, if the olefin undergoes radical polymerization easily, telomer formation will occur.    It can be minimized by use of a large excess of the thiol    In kinetic terms,* propagation becomes important if the rate of the

---

\* Considerable attention from the kinetic point of view has been given to the relationship between chain transfer and propagation in radical polymerization of olefins in the presence of thiols.  A discussion of this work is considered to be outside the scope of this chapter    For pertinent references see Walling[44] (also ref. 45, Chapters 4 and 7), Hiatt and Bartlett,[48] Gregg, Alderman, and Mayo[89]

[44] Walling, *J. Am. Chem. Soc.*, **70**, 2561 (1948).

[45] Hiatt and Bartlett, *J. Am. Chem. Soc.*, **81**, 1149 (1959).

[89] Gregg, Alderman, and Mayo, *J. Am. Chem. Soc.*, **70**, 3740 (1948)

reaction of the intermediate radical with a molecule of olefin is comparable to the rate of reaction with the thiol. The ratio of these rates has been defined as the transfer constant, $C$, and is specific for each thiol-olefin combination. Because thiol transfer constants are generally high, in

$$C = \frac{\text{rate of transfer}}{\text{rate of propagation}}$$

reaction mixtures of equimolar amounts of reactants the 1:1 adduct will predominate. Transfer constants for $n$-butanethiol and typical polymerizable olefins are shown in Table IV.

TABLE IV

TRANSFER CONSTANTS OF $n$-BUTANETHIOL AT 60°[84]

| | |
|---|---|
| Vinyl acetate | 48 |
| Styrene | 22 |
| Methyl acrylate | 1.69 |
| Methyl methacrylate | 0.67 |

An example illustrating the importance of the nature of the thiol on the rate of transfer vs. propagation is seen in the reactions of trifluoromethanethiol and methanethiol with chlorotrifluoroethylene carried out under comparable conditions (Table V).[6] Although no values have been derived, the transfer constant of trifluoromethanethiol is obviously much lower than that of methanethiol.

TABLE V

YIELDS (%) OF ADDUCTS IN ULTRAVIOLET-INITIATED ADDITIONS OF $CH_3SH$ AND $CF_3SH$ TO $CFCl{=}CF_2$

| | 1:1 Adduct (%) | 2:1 Adduct (%) | 3:1 Adduct (%) |
|---|---|---|---|
| $CH_3SH$ | 84 | 5 | — |
| $CF_3SH$ | 62 | 20 | 3 |

Other olefins that have been reported to give telomers in thiol additions are tetrafluoroethylene ($CF_3SH$[6] and $C_2H_5SH$[87]), trifluoroethylene ($CF_3SH$),[6] acrylic esters ($C_2H_5SH$,[69] $n$-$C_3H_7SH$,[69] $n$-$C_{12}H_{25}SH$[89]), styrene ($n$-$C_{12}H_{25}SH$),[90] and methyl methacrylate ($C_6H_5SH$, $m$- and $p$-$CH_3C_6H_4SH$).[91]

[87] Hanford, U.S. pat. 2,443,003 [C.A., 42, 6841 (1948)].

[88] Ipatieff and Friedman, J. Am. Chem. Soc., 61, 71 (1939).

[89] Hachihama and Sumitomo, Technol. Repts. Osaka Univ., 7, 463 (1957) [C.A., 53, 3044 (1959)].

[90] Kharasch, Nudenberg, and Meltzer, J. Org. Chem., 18, 1233 (1953).

[91] Jacobson, U.S. pat. 2,199,799 [C.A., 34, 5968 (1940)].

*Termination.* The three reactions shown on p. 166 have been proposed as the chain termination processes for radical thiol additions,[71] but relatively little study has been devoted to them. In Table II are tabulated the over-all termination rates, determined by rotating sector techniques, of several olefin-thiol addition reactions.[79] In comparison with the rates of the corresponding addition and chain transfer steps, the termination steps are very fast, probably requiring activation energies of only a few hundred calories.[71] Since the kinetic chain lengths of thiol addition reactions are usually high, the yields of the chain termination products will be very low indeed, and generally these products have not been detected.

However, in some additions the yields of chain termination products may become appreciable. Yields up to 10% of diaryl disulfides, ArSSAr, have been found in the products from the ultraviolet-initiated additions of thiophenols to 1-chlorocyclohexene and 1-chlorocyclopentene.[92] In the photoinitiated addition of *n*-butanethiol to vinyl acetate employing a large excess of the thiol (20:1 mole ratio), isolable amounts of the cross-termination product 17 were obtained in addition to the usual 1:1 adduct.[78]

$$C_4H_9S\cdot + CH_2CO_2\overset{\overset{\displaystyle SC_4H_9\text{-}n}{|}}{C}HCH_2SC_4H_9\text{-}n \rightarrow CH_3CO_2CHCH_2SC_4H_9\text{-}n$$

$$17$$
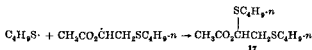
In the addition of trifluoromethanethiol to 1,1-difluorodichloroethylene, the intermediate radical formed is apparently quite stable, not readily undergoing transfer with the thiol or adding to the olefin. It dimerizes to a large degree giving the additive dimer 18 as a major product.[93]

$$CF_3S\cdot + CF_2=CCl_2 \rightarrow CF_3SCF_2CCl_2 \rightarrow (CF_3SCF_2CCl_2)_2$$

$$18$$
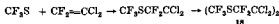
Another example of the production of the additive dimer in major proportions is seen in the reaction of thiolacetic acid with butadiene under conditions where the thiol and a stoichiometric amount of initiator (hydroxyl radicals) are added to the reaction mixture simultaneously. Under these conditions there is virtually no thiol available for chain

$$CH_3COS\cdot + CH_2=CHCH=CH_2 \rightarrow CH_3COSC_4H_6\cdot \rightarrow CH_3COS(C_4H_6)_2SCOCH_3$$

$$19$$
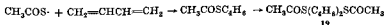
transfer and the major product is the additive dimer 19.[84]

*Stereochemistry.* The radical addition of thiols to non-cyclic olefins is not stereospecific. Apparently there is a rapid equilibration of the

[92] Goering, Relyea, and Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).
[93] Harris, J. F., Jr. Unpublished experiments.
[84] Jenner and Lindsay, *J. Am. Chem. Soc.*, **83**, 1911 (1961).

intermediate radical before the chain transfer step can occur. For example, addition of methanethiol-*d* to *cis*- and *trans*-2-butene gives the same mixture of *threo*- and *erythro*-3-deutero-2-methylthiobutanes.[95] Similarly, the addition of thiolacetic acid to both *cis*- and *trans*-2-chloro-2-butene yields the same mixture of 3-chloro-2-acetylthiobutanes under conditions where no isomerization of the olefin occurs, thus indicating a common intermediate from both olefins.[25] A rationalization for the

$$\text{CH}_3\text{COSH} + \text{CH}_3\text{CH}{=}\text{C(Cl)CH}_3 \xrightarrow{\text{UV}} \overset{\displaystyle \text{SCOCH}_3}{\underset{\displaystyle |}{\text{CH}_3\text{CHCHClCH}_3}}$$
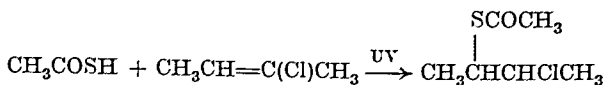
predominance of the *threo* isomer in the latter case has been offered which assumes the development of a dipole in the transition state of the transfer step and orientation of the largest negative dipole on the saturated carbon away (*trans*) from the developing dipole. This, considered with minimum steric requirements, predicts **20** (the *threo* precursor) as the transition state of lowest energy. The lack of stereospecificity in these
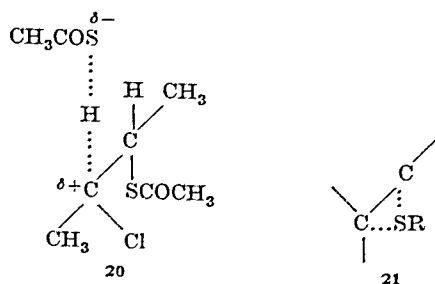


additions indicates that no bridged-type structure such as **21**, similar to that formulated in the ionic addition of sulfenyl chlorides to olefins,[96] is involved in the radical addition of thiols.

Stereospecific *trans* addition of the elements of methanethiol-*d* has been achieved at −78° in mixtures of an olefin, deuterium bromide, and methanethiol-*d*.[95] Thus *cis*- and *trans*-2-butene yield *threo*- and *erythro*-3-deutero-2-methylthiobutane, respectively. In these cases, a rapid chain transfer with deuterium bromide apparently takes place before equilibration of the intermediate radical can occur.

[95] Skell and Allen, *J. Am. Chem. Soc.*, **82**, 1511 (1960).
[96] Kharasch and Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).
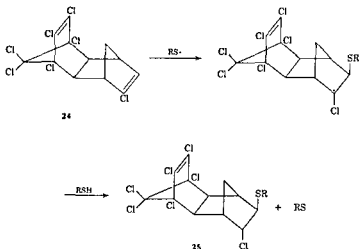
to an appreciable extent, if at all, since they should lead to exclusive *trans* addition  Since rearranged products were not observed, there is no
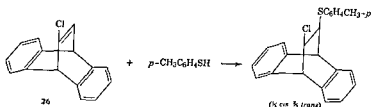


support for non-classical mesomeric type intermediate radicals such as **28** analogous to intermediates involved in ionic reactions of these bicyclic systems.
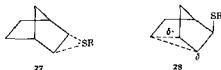


The addition of *p*-thiocresol to 2,5-norbornadiene gives two products, both having the *exo* configuration [103]  On the basis of kinetic studies it has been determined that the products arise from two separate intermediates,

[103] Cristol, Brindell, and Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958)

**29** and **30**, rather than from a single mesomeric intermediate, **31**.   Thus, after the thiyl radical adds to one of the double bonds to form the radical intermediate **29**, rearrangement to the substituted nortricyclic radical **30** occurs at a finite rate, followed by chain transfer by both radicals.   Here again there is no need to postulate (and no evidence to support) the non-classical radical intermediate **31**.
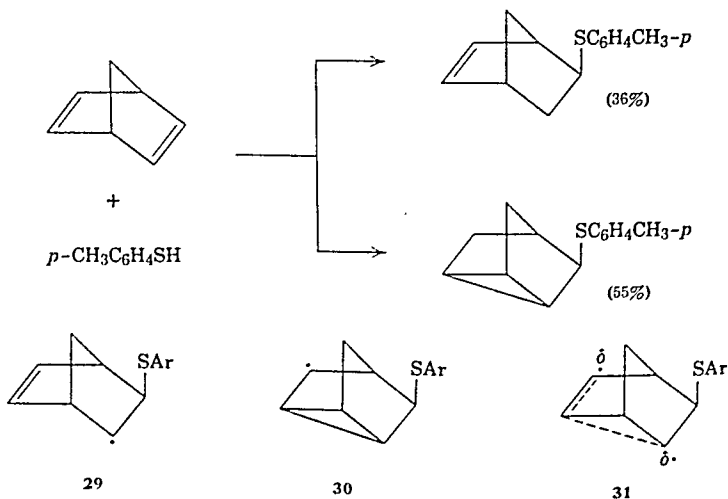


No detailed study of the stereochemistry of thiol-acetylene additions has been made.   Several products, however, have been reported which obviously arise from predominant *trans* addition.   For example, addition of cyclohexanethiol to acetylenedicarboxylic acid yielded mainly the substituted fumaric acid accompanied by a small amount of the corresponding maleic anhydride.[101]   Similarly, addition of benzyl mercaptan to propiolic

$$C_6H_{11}SH + HO_2CC\equiv CCO_2H \rightarrow$$
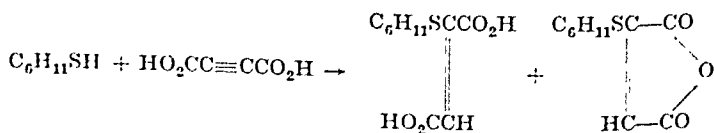


acid yielded the *cis* isomer of $\beta$-benzylmercaptoacrylic acid.[105]   The addition of ethanethiol to ethoxyethyne at $-10°$ afforded largely the *cis* isomer of 1-ethoxy-2-(ethylthio)ethylene, which partly isomerized to the *trans* isomer on distillation or long standing at room temperature.[106]

[101] Weibull, *Arkiv Kemi*, **3**, 225 (1951) [*C.A.*, **46**, 3965 (1952)].
[105] Owen and Sultanbawn, *J. Chem. Soc.*, 1949, 3109.
[106] Alkema and Arens, *Rec. Trav. Chim.*, **79**, 1257 (1960).

$$C_2H_5SH + C_2H_5OC \equiv CH \rightarrow \quad \begin{matrix} HCOC_2H_5 \\ \parallel \\ HCSC_2H_5 \end{matrix}$$
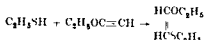
Similarly, the addition of ethanethiol to ethyl ethynyl sulfide gave the *cis* adduct [107]

The addition of a second thiol molecule is of course non-stereospecific (as in thiol-olefin additions), and both the *meso* and *dl* forms were obtained from the addition of two moles of thiolacetic acid to acetylenedicarboxylic acid [108]

$$2CH_3COSH + HO_2CC \equiv CCO_2H \rightarrow \begin{matrix} CH_3COS \quad SCOCH_3 \\ \quad | \qquad\quad | \\ HO_2CCHCHCO_2H \end{matrix}$$
$$(meso \text{ and } dl)$$
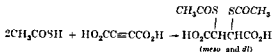
**Scope and Limitations.** *Olefins.* Radical addition of thiols to olefins and acetylenes, a reaction of extremely wide scope, has been used to prepare an enormous variety of sulfides  All types of thiol compounds, including hydrogen sulfide (p 191), thiolphosphoric acids, mono- and di-basic thiolcarboxylic acids, heterocyclic thiols, aromatic mono- and di-thiols, and alkane mono- and di-thiols enter into the reaction readily. Secondary thiols, tertiary thiols (e.g., *t*-butyl mercaptan[109],[110]), alicyclic thiols (e g , cyclohexanethiol), and alkanethiols containing the neighboring substituents OH, F, Cl, CO$_2$H, and COR all work well

Relatively few studies have been made of comparative reactivities of thiols. In studies of additions to styrene, the following order of over-all thiol reactivity has been reported:[111] ArylSH > HO$_2$CCH$_2$SH > RCH$_2$SH > RR'CHSH > RR'R''CSH. Cunneen[108],[112] observed the following order of reactivity in the addition of a series of thiols to cyclohexene, dihydromyrcene, squalene, and natural rubber: Cl$_2$CCOSH > Cl$_2$CHCOSH > ClCH$_2$COSH > CH$_3$COSH > HO$_2$CCH$_2$SH > C$_6$H$_5$SH > (CH$_3$)$_3$CHCH$_2$CH$_2$SH. This sequence roughly parallels the order of acidity of the thiols. Benzyl mercaptan is reported to be less reactive than thiolacetic acid [113]

Most olefins, linear and cyclic, undergo radical thiol addition readily. Terminally unsaturated hydrocarbons are more reactive than their internally unsaturated or cyclic counterparts, and the RS group invariably

[107] Shostakovskĭ, Prikhslaeva, Tzymbel, and Stolyarova, *J Gen Chem USSR (Engl. Transl.)*, **30**, 3116 (1960).
[108] Cunneen, *J Chem Soc*, **1947**, 36
[109] Vinton, U S pat  2,607,775 [*C A* , **47**, 6989 (1953)].
[110] Yamagishi and Nakazima, *Nippon Kagaku Zassho*, **75**, 1086 (1954) [*C.A.*, **51**, 14596 (1957).]
[111] Kharasch, Nudenberg, and Mantell, *J. Org Chem* , **16**, 524 (1951)
[112] Cunneen, *J. Chem Soc*, **1947**, 134
[113] Brown, Jones, and Pinder, *J Chem Soc*, **1951**, 3315

becomes attached to the terminal carbon atom, as in the addition of ethanethiol to propylene.[88]   Olefins with considerable branching about

$$C_2H_5SH + CH_2{=}CHCH_3 \rightarrow C_2H_5SCH_2CH_2CH_3$$
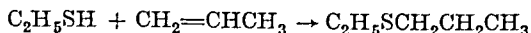
the double bond (e.g., 3-methyl-2-butene) may also be employed, and the product is that predicted from the more stable intermediate radical.[88]

$$C_2H_5SH + CH_3CH{=}C(CH_3)_2 \rightarrow C_2H_5SCH(CH_3)CH(CH_3)_2$$
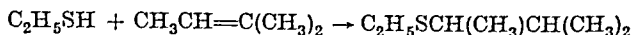
From internal olefins with similar hydrocarbon substituents, both 1:1 adducts are obtained.   Thus nearly equal amounts of the two possible thiolacetates are obtained in the addition of thiolacetic acid to 2-pentene.[114]

$$CH_3COSH + CH_3CH{=}CHC_2H_5 \rightarrow CH_3COS\overset{\overset{\displaystyle CH_3}{|}}{C}HC_3H_7{\text{-}}n + CH_3COSCH(C_2H_5)_2$$
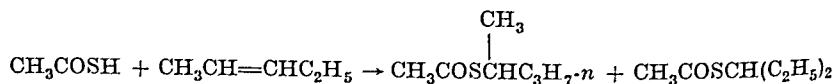
Unsaturated thiols (e.g., allyl mercaptan,[115,116] crotyl mercaptan,[115] 3-mercaptocyclopentene,[115] 4-mercapto-1-butene,[115] 5-mercapto-1-pentene,[115] cinnamyl mercaptan,[117] 4-mercaptoethylcyclohexene,[118] and 3-methyl-2-butene-1-thiol[115]) have been reported to undergo self-addition, usually spontaneously.   Neither the reactions nor the products have received extensive investigation.

$$CH_2{=}CHCH_2SH \rightarrow {+}(CH_2CH_2CH_2S{)}{+}_x$$
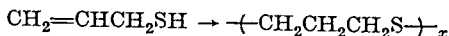
Ethylenes with a variety of substituents containing hetero atoms have been used.   The product is that shown in the accompanying equation.

$$RSH + CH_2{=}CHX \rightarrow RSCH_2CH_2X$$
$$(X = RCO_2, HOCH_2, RO, RS, R_3Si, (RO)_3B, NO_2, RSO_2, RCOS)$$
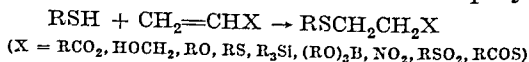
Addition of trifluoromethanethiol to tetrafluoroethylene yields a series of telomers with the 1:1 adduct predominating.[6]   The addition of thiols to

$$CF_3SH + CF_2{=}CF_2 \xrightarrow{\text{UV}} CF_3S(CF_2CF_2)_nH$$
$$(n = 1, 2, 3)$$
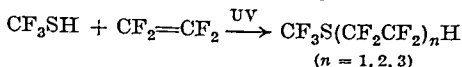
other highly fluorinated but unsymmetrical terminal olefins generally leads to a single 1:1 adduct whose orientation can be predicted from the more stable intermediate radical.[6,119]   Addition of methanethiol, trifluoromethanethiol, and 2,2,2-trifluoroethanethiol to hexafluoropropene, however, yields both 1:1 adducts, the relative amounts depending on the

[114] Hewett, W. A., Doctoral Dissertation, Northwestern University, 1955; *Dissertation Abstr.*, **16**, 24 (1956).

[115] vonBraun and Plate, *Ber.*, **67**, 281 (1934).

[116] Ayers and Scott, U.S. pat. 2,738,341 [*C.A.*, **50**, 11720 (1956)].

[117] vonBraun and Murjahn, *Ber.*, **59**, 1202 (1926).

[118] Marvel and Olson, *J. Polymer Sci.*, **26**, 23 (1957).

[119] W. L. Thompson, Doctoral Dissertation, Cornell University, 1955; *Dissertation Abstr.*, **16**, 243 (1956).

$$RSH + CF_2=CFCF_3 \xrightarrow{\text{UV or x-ray}} \underset{32}{RSCF_2CHFCF_3} + \underset{33}{RSCFCHF_2}$$
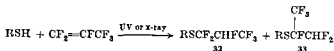
nature of the thiol (Table VI) [6] Consideration of the stabilities of intermediate radicals leads to the prediction of 32 as the favored product, but in fact 33 is the predominant adduct from trifluoromethanethiol A correlation between the relative electrophilicities ($CF_3S\cdot > CF_3CH_2S >$ $CH_3S\cdot$) of the adding radical and the relative abundance of adduct 33,

TABLE VI

1.1 ADDUCT COMPOSITION FROM ADDITION OF
THIOLS (RSH) TO HEXAFLUOROPROPENE

| R | 1.1 Adduct Composition | |
|---|---|---|
| | 32 (%) | 33 (%) |
| $CF_3$ | 45 | 55 |
| $CF_3CH_2$ | 70 | 30 |
| $CH_3$ | 92 | 8 |

whose formation requires attachment of the thiyl radical to the negatively polarized carbon of hexafluoropropene (34), can be made.[6] One attempt to add a thiol to an internal perfluoroolefin (perfluoro-2 butene) failed.[6]

$$\overset{\delta-}{CF_3}CF=\overset{\delta+}{CF_2}$$
$$34$$

Other highly halogenated olefins have scarcely been studied, although additions occur readily to vinyl chloride[120] and to other olefins with one chlorine atom on the double bond [92] The ultraviolet-initiated addition of thiophenol to 3,3,3 trichloropropene proceeds with a rearrangement that apparently involves migration of a chlorine atom in the intermediate radical [121]

$$C_6H_5S\cdot + Cl_3CCH=CH_2 \longrightarrow Cl_3CCHCH_2SC_6H_5$$

$$\Big\downarrow \text{Rearrangement}$$

$$Cl_2CHCHClCH_2SC_6H_5 \longleftarrow Cl_2CCHClCH_2SC_6H_5$$
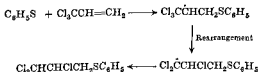
A similar rearrangement was observed in the reaction of benzyl mercaptan with this olefin.

120 Hoshino and Yamaguchi, Jap pat. 6,480 [C A., 49, 9689 (1955)]

121 Nesmeyanov, Freidlina, Petrova, and Terent'eva, Proc. Acad. Sci USSR, Chem Sect.
(Engl Transl.), 127, 591 (1959).

Radical addition of thiols to $\alpha,\beta$-unsaturated carbonyl compounds and nitriles gives the 1:1 adduct with the RS group on the $\beta$-carbon atom. The same adduct is obtained when the reaction proceeds by a polar mechanism. The two pathways have been studied separately with ethanethiol and methyl acrylate, which, when mixed in the absence of a catalyst, do not react.[69] If a small amount of ascaridole is added and the mixture irradiated, an exothermic reaction ensues yielding methyl 2-ethylthiopropionate and telomers containing two, three, and more molecules of methyl acrylate. If, instead of peroxide, a small amount of trimethylbenzylammonium hydroxide ("Triton B") is added, a rapid reaction takes place which produces the 1:1 adduct in 95% yield. Since

$$C_2H_5SH + CH_2{=}CHCO_2CH_3 \begin{array}{c} \xrightarrow{\text{Peroxide}}_{\text{UV}} \quad C_2H_5SCH_2CH_2CO_2CH_3 + \\ \qquad\qquad C_2H_5S[CH_2CH(CO_2CH_3)]_nH \\ \\ \xrightarrow{\text{Base}} \quad C_2H_5SCH_2CH_2CO_2CH_3 \end{array}$$
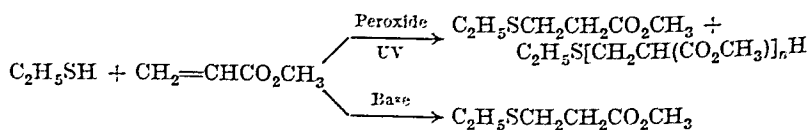
no reaction occurs unless a catalyst is added, it is possible to direct the reactants into either a radical or ionic reaction. However, many analogous reactions occur without the addition of a catalyst, and in most of them it has not been determined whether the reaction follows an ionic or a free radical pathway.[122–149]

Radical addition of thiophenol to benzothiophene-1-dioxide produces the 2-substituted sulfide 35, presumably because of the resonance stabilization

possible in the intermediate benzyl-type radical [141] Under base catalysis, the 3-substituted sulfide 36 is obtained. Aliphatic thiols under all conditions give the 3-sulfide
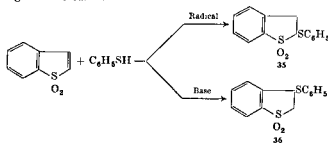


Additions of thiol acids, mainly thiolacetic acid, to a series of unsaturated ketosteroids (e g , $\Delta^{1\,4}$-3-oxo-, $\Delta^{4\,6}$-3-oxo-, and $\Delta^{1\,4\,6}$-3-oxo-steroids) have been reported. In view of the rather specialized nature of the compounds involved, these additions, which are all tabulated in two articles,[142,143] are not included in the table of thiol acid additions.

Several monoolefinic compounds have been reported to be inert to radical thiol additions Thiolacetic acid failed to add to stilbene in the presence of peroxide [141] Similarly, thiolacetic acid failed to react with cinnamyl alcohol,[141] but the ascaridole-catalyzed addition of benzyl mercaptan proceeded in 47% yield [113] Methyl cinnamate was reported not to react with $p$-thiocresol or benzyl mercaptan,[123] yet cinnamic acid formed an adduct with benzyl mercaptan in the presence of peroxide.[113]

Non-conjugated dienes (e g , dihydromyrcene) furnish mono- and diadducts,[73] the relative amounts depending on the ratio of the reactants.

$$CH_3COSH + (CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_3 \rightarrow$$
$$(CH_3)_2C=CH(CH_2)_2CH(CH_3)CH(CH_3)SCOCH_3$$
$$+ (CH_3)_2CHCH(SCOCH_3)(CH_2)_2CH(CH_3)CH(CH_3)SCOCH_3$$
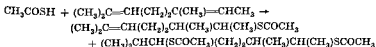
Conjugated dienes undergo 1,4 addition only.[145,146] The geometry of the

$$n \; C_4H_9SH + C_2H_5CH=CHCH=CH_2 \xrightarrow{\text{Persulfate}} n \; C_4H_9SCH_2CH=CHCH_3$$

diene apparently makes no difference in the choice of 1,4 over 1,2 addition, since both 1,2-dimethylenecyclohexane and 3-methylenecyclohexene gave only 1,4 adducts [147]

[141] Bordwell, Chapman, and McKellin, J Am Chem Soc , 76, 3637 (1954).
[142] Dodson and Tweit, J Am Chem Soc , 81, 1224 (1959).
[143] Tweit and Dodson, J. Org Chem , 24, 277 (1959).
[144] Brown, Jones, and Pinder, J. Chem Soc 1951, 2123
[145] Longfield, Jones, and Sivertz, Can J , Res , 269, 373 (1950)
[146] Marvel and Cripps, J Polymer Sci , 8, 313 (1952).
[147] Cristol and Nagpal, J Org Chem , 26, 365 (1961).

If the reaction is forced so that a second mole of thiol adds, a rearrangement occurs and the product is a 1,4-bis-sulfide.[148,149] The nature of

$$p\text{-}CH_3C_6H_4SH + $$



$$p\text{-}CH_3C_6H_4SH + $$
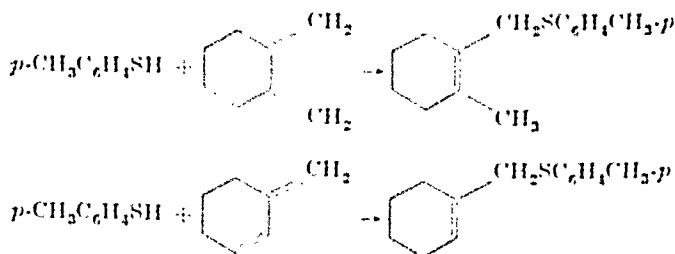


this rearrangement is not understood.

$$p\text{-}CH_3C_6H_4SH + p\text{-}CH_3C_6H_4SCH_2CH \cdot \cdot CHCH_3 \xrightarrow[\text{or UV}]{\text{Peroxide}}$$

$$p\text{-}CH_3C_6H_4S(CH_2)_4SC_6H_4CH_3\text{-}p$$
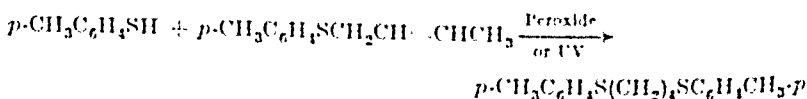
Radical additions of dithiols to diolefins lead to polymeric materials.[118,150,151] The dithiols which have been used include aliphatic dithiols,[148] aromatic dithiols,[152] and dibasic aliphatic and aromatic thiol acids.[153] The diolefins employed have generally been non-conjugated; e.g., biallyl. Most widely studied is the biallyl-hexamethylenedithiol system which leads to the formation of polyhexamethylene sulfide.[154,155]

$$HS(CH_2)_6SH + CH_2\!\!=\!\!CH(CH_2)_2CH\!\!-\!\!CH_2 \rightarrow +S(CH_2)_6S(CH_2)_6\!\!+\!\!_x$$
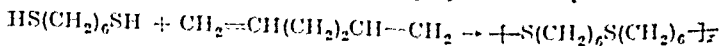
Conjugated olefins are generally unsatisfactory since the initial 1,4 addition gives allyl type sulfides which do not undergo further addition readily. Thus the reaction of hexamethylenedithiol with 1,3-butadiene leads to the formation of 1,6-bis-(crotylmercapto)hexane, which is inert to further reaction.[146] Similarly, allyl sulfide does not form polymers with hexamethylenedithiol,[146,156] but allyl ether does.[146]

$$HS(CH_2)_6SH + CH_2\!\!=\!\!CHCH\!\!=\!\!CH_2 \rightarrow$$

$$\begin{array}{c} CH_3CH\!\!=\!\!CHCH_2\!\!-\!\!S \\ | \\ (CH_2)_6 \\ | \\ CH_3CH\!\!=\!\!CHCH_2\!\!-\!\!S \end{array}$$
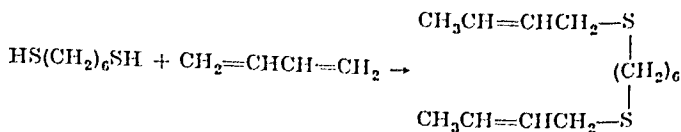
[148] Marvel and Chambers, J. Am. Chem. Soc., 70, 993 (1948).
[149] J. A. Reeder, Doctoral Dissertation, Dissertation Abstr., 20, 3960 (1960).
[150] Marvel, Record Chem. Progr. (Kresge-Hooker Sci. Libr.), 12, 185 (1951).
[151] Marvel, Hinman, and Inskip, J. Am. Chem. Soc., 75, 1097 (1953).
[152] Marvel and Caesar, J. Am. Chem. Soc., 73, 1097 (1951).
[153] Marvel and Kotch, J. Am. Chem. Soc., 73, 1100 (1951).
[154] Marvel and Markhart, J. Am. Chem. Soc., 73, 1064 (1951).
[155] Marvel and Aldrich, J. Am. Chem. Soc., 72, 1978 (1950).
[156] Marvel and Markhart, J. Polymer Sci., 6, 711 (1951).

When thiols, olefins, and carbon monoxide are heated at 3000 atm. pressure with a peroxide catalyst, aldehydes are produced in addition to the olefin-thiol adduct.[81] For example, propylene, ethanethiol, carbon monoxide, and di-$t$-butyl peroxide at 130° produce 3-ethylthio-2 methylpropanal (16%) and ethyl $n$-propyl sulfide (50%) Likely steps in the reaction leading to the aldehyde are shown in the accompanying equations.

$$C_2H_5S + CH_2=CHCH_3 \rightarrow \begin{matrix} CH_3 \\ | \\ C_2H_5SCH_2CH \end{matrix}$$

$$\begin{matrix} CH_3 \\ | \\ C_2H_5SCH_2CH \end{matrix} + CO \rightarrow \begin{matrix} CH_3 \\ | \\ C_2H_5SCH_2CHCO\cdot \end{matrix}$$

$$\begin{matrix} CH_3 \\ | \\ C_2H_5SCH_2CHCO\cdot \end{matrix} + C_2H_5SH \rightarrow \begin{matrix} CH_3 \\ | \\ C_2H_5SCH_2CHCHO \end{matrix} + C_2H_5S$$
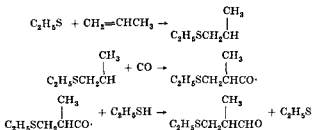
*The Oxidative Addition of Thiols to Olefins.* When the addition of thiols to olefins is carried out with oxygen supplied to the reaction mixture, oxygen participates in the reaction and the initial product is a $\beta$-hydroperoxy sulfide. A probable pathway is shown in the following equations

$$RSH \xrightarrow{O_2} RS\cdot + HOO$$

$$RS\cdot + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C} \rightarrow RS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\cdot$$

$$RS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\cdot + O_2 \rightarrow RS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}OO\cdot$$

$$RS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}OO\cdot + RSH \longrightarrow RS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}OOH + RS$$
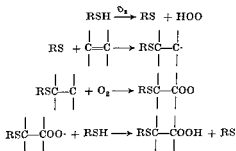
The hydroperoxide usually rearranges in the reaction mixture to the isomeric $\beta$-hydroxy sulfoxide, and this is the major product isolated The corresponding $\beta$-hydroxy sulfide, the conventional thiol olefin adduct, and the disulfide derived from the thiol are often obtained as byproducts. The products isolated from the reaction of $n$-propanethiol, styrene, and oxygen are shown in the accompanying equation.[111]

$$C_6H_5CH=CH_2 + n\text{-}C_3H_7SH + O_2 \rightarrow$$
$$C_6H_5CHOHCH_2S(O)C_3H_7\text{-}n + C_6H_5CHOHCH_2SC_3H_7\,n$$
$$+ C_6H_5CH_2CH_2SC_3H_7\text{-}n + (n\text{-}C_3H_7)_2S_2$$
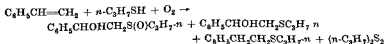
Reduction of the crude hydroperoxide from the reaction of indene, thiophenol, and oxygen gives *trans*-2-phenylmercapto-1-indanol, indicating that the peroxide has the *trans* configuration and that the attack by oxygen on the intermediate radical 37 occurs *trans* to the RS group.[157]    Re-



37
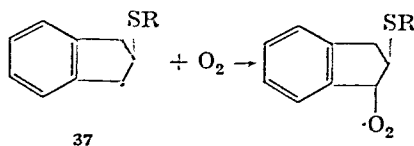
arrangement of this hydroperoxide to the hydroxy sulfoxide gave the two isomers of *trans*-2-phenylsulfinyl-1-indanol.

The initially formed hydroperoxide 38 from the reaction of indene, 2-naphthalenethiol, and oxygen has been isolated in crystalline form (m.p. 70°), characterized,[158,159] and its decomposition to 2-(2-naphthyl-sulfinyl)-1-indanol (39) in benzene solution observed.    When the decomposition was carried out in the presence of 2-(4-chlorophenylmercapto)-1-indanol, no oxidation of the indanol was detected.    This observation



38                    39
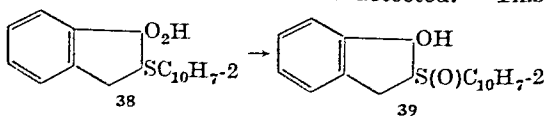
suggests that the conversion of 38 to 39 is an intramolecular rearrangement.[159]    On the other hand, the crude hydroperoxide from thiophenol, indene, and oxygen is reported to rearrange to the sulfoxide by a second-order process,[157] suggesting an intermolecular oxidation analogous to the well-known bimolecular hydroperoxide oxidation of sulfides to sulfoxides.[160,161]

The reaction to give $\beta$-hydroxy sulfoxides is reported to be strongly accelerated by chloride and bromide salts.[162,163]    Particularly effective are amine hydrochlorides and hydrobromides, but sodium and potassium bromides and chlorides are also effective.    Iodides are inhibitory.    The mechanism of this catalysis is not clear.    Ultraviolet radiation has been used to initiate oxidative additions of *n*-dodecanethiol.[159]

When the reaction of indene, thiols, and oxygen is carried out in the presence of alkyl amines, hydroxy sulfides and not sulfoxides are obtained,

[157] Ford, Pitkethly, and Young, *Tetrahedron*, 4, 325 (1958).
[158] Oswald, *J. Org. Chem.*, 24, 443 (1959).
[159] Oswald, *J. Org. Chem.*, 26, 842 (1961).
[160] Overberger and Cummins, *J. Am. Chem. Soc.*, 75, 4250 (1953).
[161] Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. II, pp. 64–66, Chemical Publishing Co., Inc., New York, 1960.
[162] Bredereck, Wagner, Kottenhahn, *Chem. Ber.*, 93, 2415 (1960).
[163] Bredereck, Wagner, and Kottenhahn, *Angew. Chem.*, 70, 73 (1958).

presumably by intermediate formation of hydroperoxy sulfides followed by an amine-catalyzed oxidation of additional thiol by the hydroperoxide [164]
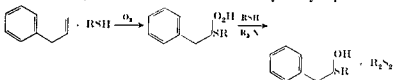


The scope of the oxidative addition of thiols to olefins has barely been explored    Both alkanethiols and aromatic thiols have been used    The olefins thus far used include styrene,[159,162] indene,[159] methacrylonitrile,[162] methyl acrylate,[162] 1 hexene,[165] 1-octene,[114] bicyclopentadiene,[166] and Aldrin [166]

A related group of oxidative additions are the reactions of thiols with oxygen and anthracene or substituted anthracenes    The principal products are 9,10-dihydro-9,10-disubstituted anthracenes [167-169]    For example, thiolacetic acid, oxygen, and anthracene give as the major products two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (40), along with 9-(acetylthio)anthracene and a small amount of di-(9-anthryl)disulfide [169]

$$CH_3COSH + O_2 +$$



40
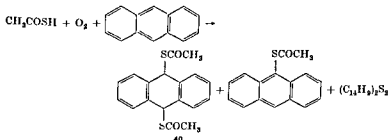
It has been postulated that all these products arise from an initially formed hydroperoxide 41[169] (see formula at top of p 188).

*Acetylenes.* The radical addition of thiols to acetylenes with a variety of substituents (e g , alkyl, aryl, carboxyl, α-hydroxyalkyl, α-haloalkyl, alkoxy, and alkylthio) proceeds readily to give monoadducts, diadducts, or both, depending on the relative proportions of the starting materials.

[164] Oswald, Noel, and Fisk, *J Org Chem*, **26**, 3974 (1961)

[165] Harman, U S pat. 2,515,120 [*C.A* , **44**, 8942 (1950)]

[166] Oswald and Noel, *J Org. Chem* , **26**, 3948 (1961)

[167] Mikhailov and Blokhina, *Doklad Akad Nauk SSSR*, **80**, 373 (1951) [*C.A* , **46**, 5025 (1952)]

[168] Mikhailov and Blokhina, *Probl. Mekhanizma Org. Reaktsu Akad. Nauk, Ukr. SSR, Otdel Fiz -Mat i Khim Nauk*, 1953, 215 [*C A* , **50**, 16735 (1956)]

[169] Beckwith and Low, *J. Chem Soc* , **1961**, 1304

Generally, the first molecule of thiol adds more readily than the second. Only monoadducts are obtained from dimethyl acetylenedicarboxylate and ethanethiol,[170] $p$-methoxyphenylacetylene and thiolacetic acid,[171]



**41**
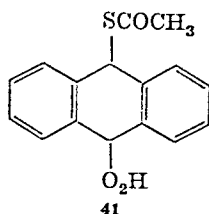
3-methyl-3-hydroxy-1-butynyl ethyl ether and ethanethiol,[172] and 4-hydroxy-1-pentyne[173] or phenylacetylene and thiolacetic acid.[171] Addition of the first molecule of thiol proceeds in the anti-Markownikoff manner, forming the abnormal product. The second molecule of thiol generally adds to yield the diadduct with the thio groups on adjacent carbon atoms.[170,174,175] Additions to phenylacetylene, however, lead to

$$CH_3COSH + HC{\equiv}CCH_2OH \longrightarrow$$

$$CH_3COSCH{=}CHCH_2OH \xrightarrow{CH_3COSH} \begin{matrix} CH_3COSCH_2CHCH_2OH \\ | \\ SCOCH_3 \end{matrix}$$
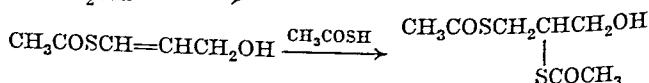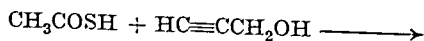
products in which both RS groups are attached to the $\beta$-carbon atom, presumably because of the large resonance stabilization possible in the intermediate benzyl-type radicals.[170]

$$C_2H_5SH + C_6H_5C{\equiv}CH \xrightarrow[\text{UV}]{\text{Peroxide}} C_6H_5CH_2CH(SC_2H_5)_2$$
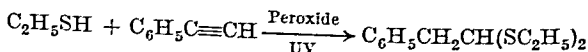
The reaction of ethanedithiol with 2-butyne-1,4-diol diacetate involves cyclization and yields 1,2-bis-(acetoxymethyl)-1,4-dithiane (**42**) in addition to polymer.[170]

$$HSCH_2CH_2SH + CH_3CO_2CH_2C{\equiv}CCH_2OCOCH_3 \xrightarrow[\text{UV}]{\text{Peroxide}}$$



$+$ polymer

**42**
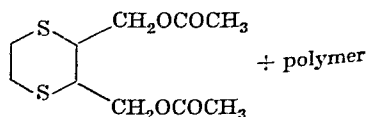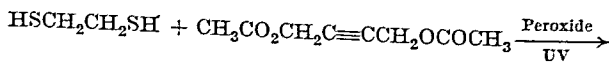
[170] Blomquist and Wolinsky, J. Org. Chem., 23, 551 (1958).

[171] Bader, Cross, Heilbron, and Jones, J. Chem. Soc., 1949, 619.

[172] Weiland and Arens, Rec. Trav. Chim., 75, 1358 (1956).

[173] Bader, J. Chem. Soc., 1956, 116.

[174] Yamagishi, Tanaka, and Hoshino, Bull. Chem. Soc. Japan, 30, 455 (1957) [C.A., 52, 8952 (1958)].

[175] Sauer, J. Am. Chem. Soc., 79, 5314 (1957).

The peroxide-initiated reactions of acetylene with carbon monoxide and thiols lead to the formation of bis-sulfides and aldehydes, in a manner analogous to the corresponding olefin reaction discussed on p 185 [175]

$$RSH + CO + HC\!\!=\!\!CH \rightarrow RSCH_2CH_2SR + RSCH\!\!=\!\!CHCHO$$
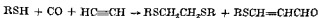
**Experimental Conditions.**  Conditions used in radical thiol additions are usually defined by the initiator employed  Peroxides are the most widely employed initiators  Often the peroxides present in the olefin are sufficient to initiate the reaction, possibly by a redox reaction with the thiol.  For example, in many addition reactions of thioglycollic acid and thiophenol, an exothermic reaction ensues upon mixing the reactants.  The peroxides used include ascaridole, benzoyl peroxide, di-t-butyl peroxide, and potassium persulfate.[145]

The mixture of reactants, containing the catalyst in amounts varying from a few tenths of a per cent to a few per cent, is usually heated to the decomposition temperature of the catalyst either in an open vessel or, in the case of volatile reactants, in a sealed metal or glass container  In some reactions the peroxides are decomposed by ultraviolet irradiation.[69,119,170,172,176]

Inorganic reducing agents, e g , ferrous chloride and chromous chloride, have also been employed to decompose peroxides (redox systems), thus initiating addition at room temperature.[177]  Redox systems comprising persulfate and bisulfite have been used extensively in the reactions of dithiols with dienes to produce polymers [150]  Oxygen in small amounts has been employed for initiation[178-180] and may actually be the initiator in many additions reported to occur spontaneously when no precautions are taken to exclude air  When substantial quantities of oxygen are made available to the reaction mixture, oxygen-containing products are formed.  Azonitriles, e g , azobis(isobutyronitrile), have also been employed extensively to catalyze thiol additions, and the conditions are analogous to those used in peroxide-catalyzed reactions  The initiators are generally decomposed thermally, and less frequently by ultraviolet radiation.[174,181]

Several forms of radiant energy, e g , ultraviolet radiation, x-rays, $\gamma$-rays and $\beta$-rays, have been used for initiating thiol addition reactions  Ultraviolet radiation (below 3000 Å) is most commonly used  Initiation by ultraviolet radiation probably can also occur by the photodecomposition

[175] Ruhlmann, Schrapler, and Cramer, *J. Prakt Chem*, [4] 10, 325 (1960)

[177] Hoffelman and Berkenbosch, US patent 2,352,435 [*C A*, 38, 5506 (1944)].

[178] Ellington, US pat 2,423,641 [*C A*, 42, 3774 (1948)]

[179] Shostakovskii, Prileshaeva, and Uvarova, *Bull. Acad Sci, USSR, Div Chem. Sci. (Engl. Transl)*, 1954, 447

[180] Vesterman and Frenkel, Fr pat 1,103,763 [*C A*, 52, 18220 (1958)]

[181] Theobald, US pat 2,675,392 [*C A*, 49, 4722 (1955)].

of peroxides contained in the reactants, and this may be the mechanism for initiation by radiation of wavelengths greater than 3000 Å. The reactants generally are contained in sealed or open transparent vessels and exposed to an ultraviolet source at ambient temperature. With very low-boiling reactants, e.g., fluoroölefins, irradiation of the reactants at reflux has been employed.[6] Generally, radiation of 3000 Å or lower is employed, necessitating the use of Vycor or quartz containers. However, many reactions have been reported to proceed in a satisfactory manner when a commercial sunlamp and Pyrex equipment are used.

Ultraviolet radiation above 3000 Å has frequently been used in conjunction with photosensitizers such as acetone,[182] mercury salts.[183,184] organic disulfides,[90,109,185–187] and lead tetraalkyls.[188] X-rays have been used to initiate additions of thiols to fluoroölefins,[6] and both x-rays and $\gamma$-rays have been employed in the addition of $n$-butanethiol to 1-pentene.[72,73] In these reactions the reactants, contained in stainless steel pressure vessels or Pyrex tubes, were exposed to x-rays or $\gamma$-rays at ambient temperatures for periods of several hours. $\beta$-Radiation from an $Sr^{90}$-$Y^{90}$ source has been employed to initiate the reaction of $n$-butanethiol and 1-octene contained in a Pyrex reactor.[74]

In the formation of polymers from dithiols and non-conjugated olefins, emulsion polymerization techniques employing exactly equimolecular amounts of the reactants and a bisulfite-persulfate-copper initiator system have given products having the highest molecular weights.[154,155] Other initiators, e.g., peroxides, azonitriles, and ultraviolet radiation, have also been studied.

Oxidative additions of thiols to olefins are generally carried out by shaking the reactants in a hydrocarbon solvent in an atmosphere of oxygen or with air bubbling through at ambient temperatures.[111,157] Periods of time vary from an hour to several days. In experiments with anthracene when oxygen absorption was slow, catalytic quantities of cumene hydroperoxide and ferrous sulfate were added.[169] When it is desired to stop the reaction at the hydroperoxide stage, the reactions are preferably carried out at 0° for a few hours.[159] The amine hydrohalide-catalyzed experiments are carried out in essentially the same manner except that a per cent or less of dibutylamine hydrochloride or hydrobromide is added.[162]

[182] Barnard, Fabian, and Koch, *J. Chem. Soc.*, **1949**, 2442.
[183] Kaneko and Mii, *J. Chem. Soc. Japan*, **59**, 1382 (1938) [*C.A.*, **33**, 2106 (1939)].
[184] Yamagishi, Tanaka, and Hoshino, *Bull. Chem. Soc. Japan*, **29**, 447 (1956).
[185] Rueggeberg, Cook, and Reid, *J. Org. Chem.*, **13**, 110 (1948).
[186] Ellingboe, U.S. pat. 2,439,203 [*C.A.*, **42**, 5046 (1948)].
[187] Rueggeberg and Cook, U.S. pat. 2,810,687 [*C.A.*, **52**, 3850 (1958)].
[188] Evans, Vaughan, and Rust, U.S. pat. 2,411,961 [*C.A.*, **41**, 2068 (1947)].

### Addition of Hydrogen Sulfide to Olefins

In the presence of ultraviolet radiation or certain free radical initiators, hydrogen sulfide adds to olefins in the abnormal manner to yield mixtures of thiols and sulfides

$$H_2S + CH_2 = CHR \rightarrow RCH_2CH_2SH + (RCH_2CH_2)_2S$$
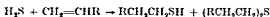
Although no detailed study of the mechanism has been made, it seems certain that these reactions occur via a radical chain mechanism fully analogous to that substantiated for thiol additions. In the products

$$H_2S \xrightarrow{\text{Initiation}} HS$$

$$HS + RCH = CH_2 \longrightarrow R\dot{C}HCH_2SH$$

$$R\dot{C}HCH_2SH + H_2S \longrightarrow RCH_2CH_2SH + HS$$

$$RCH_2CH_2S \longrightarrow RCH_2CH_2S$$

$$RCH_2CH_2S + CH_2 = CHR \longrightarrow RCH_2CH_2SCH_2\dot{C}HR$$

$$RCH_2CH_2SCH_2\dot{C}HR + H_2S \longrightarrow RCH_2CH_2SCH_2CH_2R + HS$$
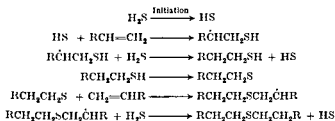
whose structures have been determined, the SH group is found on the carbon atom normally attacked by radicals, e.g., the terminal carbon in terminal olefins. Formation of the sulfide occurs by a typical thiol-olefin addition reaction. As in thiol additions, the photoinitiated addition of hydrogen sulfide to 1-chlorocyclohexene is predominantly trans, the 1:1 adduct consisting of 85–90% cis-2-mercapto-1-chlorocyclohexane.[97] Other aspects of the mechanism and stereochemistry have apparently not been investigated.



(85–90% cis, 10–15% trans)
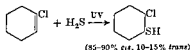
Radical addition of hydrogen sulfide to olefins is a general reaction applicable to terminal, internal, and cyclic olefins. Ethylene and hydrogen sulfide, at temperatures of 160–200° and pressures of 600–1000 atm , react to form a mixture of ethanethiol, diethyl sulfide, and ethyl butyl sulfide.[188] In an azonitrile-initiated reaction of hydrogen sulfide, carbon monoxide, and ethylene, the hydrogen sulfide added to ethylene to give ethanethiol, which was subsequently converted to diethyl sulfide and 2-ethylmercaptopropionaldehyde dithioacetal.[81]

$$CH_2 = CH_2 + CO + H_2S \xrightarrow{\text{Azonitrile}} (C_2H_5)_2S + C_2H_5SCH_2CH_2CH(SC_2H_5)_2$$

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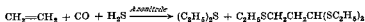
[188] Harmon, U.S pat 2,380,099 [C.A , 40, 1865 (1946)]

Terminal olefins are the most reactive in radical hydrogen sulfide additions, but highly branched internal olefins, e.g., 2,3-dimethyl-2-butene, also react.[190]  Reactions of equimolecular amounts of hydrogen

$$H_2S + (CH_3)_2C=C(CH_3)_2 \rightarrow (CH_3)_2CHC(CH_3)_2 + [(CH_3)_2CHC(CH_3)_2]_2S$$

with an SH group on the middle carbon.
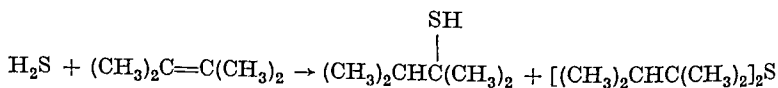
sulfide and dienes such as diallyl ether lead to polymers of low molecular weight.[191]  With an appreciable excess of hydrogen sulfide, both a

$$(CH_2=CHCH_2)_2O + H_2S \xrightarrow{UV} H[S(CH_2)_3O(CH_2)_3]_n SH$$

(Av. mol. wt. = 674)
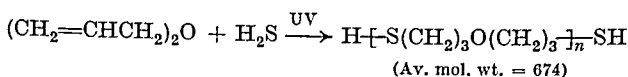
monothiol and dithiols are obtained from bicyclo[2.2.1]hepta-2,5-diene[192] and 2,5-dimethyl-2,4-hexadiene.[193]  The reaction of hydrogen sulfide

$$H_2S + (CH_3)_2C=CHCH=C(CH_3)_2 \rightarrow$$

$$(CH_3)_2CHCHCH=C(CH_3)_2 \quad + \quad (CH_3)_2CHCHCHCH(CH_3)_2$$
$$\underset{SH}{|} \qquad\qquad\qquad \underset{HS \quad SH}{|\quad |}$$
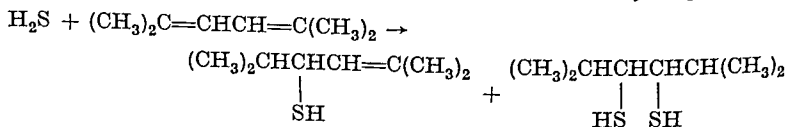
with 3,7-dimethyl-2,6-octadiene gave, in addition to two monothiols and a dithiol, a thiopyran **43** resulting from intramolecular sulfide formation.[194]

$$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_3 \xrightarrow[\text{(Acetone)}]{UV}$$



**43**
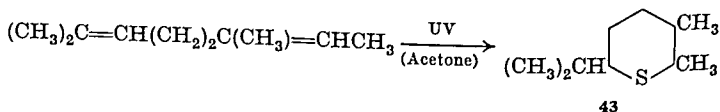
Additions of hydrogen sulfide to ethylenes with hetero atom substituents such as Cl, SiR$_3$, SR, OR, or NR$_2$ generally lead to products with the sulfur atom attached to the CH$_2$ group.  Additions to vinyl ethers have been the most extensively examined.[195]  In a study of the oxygen-initiated addition of hydrogen sulfide to ethyl, isopropyl, isobutyl, isopentyl, n-octyl, and cyclohexyl vinyl ether, the rate of addition was observed to decrease as the alkyl group became longer and more branched.[196,197] From all the olefins except cyclohexyl vinyl ether, both the thiol and the

[190] Pinkney, U.S. pat. 2,551,813 [C.A., 45, 9559 (1951)].

[191] Vaughan and Rust, J. Org. Chem., 7, 472 (1942).

[192] Mahan and Louthan, U.S. pat. 3,019,267 [C.A., 56, 12774 (1962)].

[193] May and Lee, U.S. pat. 2,960,538. [C.A., 55, 9280 (1961)].

[194] Naylor, J. Chem. Soc., 1947, 1532.

[195] Shostakovskiĭ, Shapiro, and Dubrova, J. Gen. Chem. USSR (Engl. Transl.), 28, 3337 (1958).

[196] Shostakovskiĭ, Prilezhaeva, and Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1954, 235.

[197] Shostakovskiĭ, Prilezhaeva, and Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1954, 245.

Generally speaking, if a high yield of the thiol is desired, a high ratio of hydrogen sulfide to olefin is necessary. Conversely, for a high yield of sulfide the ratio of olefin to hydrogen sulfide should be high. It has been reported that the presence of water increases the ratio of thiol to sulfide,

TABLE VII

ASCARIDOLE-INITIATED ADDITION OF HYDROGEN
SULFIDE TO $n$-BUTYL VINYL ETHER

| Molar Ratio of $H_2S$:Olefin | Ratio of Yield Thiol:Sulfide |
|---|---|
| 0.37 | 0.081 |
| 1.55 | 1.9 |
| 1.98 | 3.5 |
| 2.13 | 5.6 |

other factors being constant.[201] The polymer from hydrogen sulfide and diallyl ether has the highest molecular weight when an exact 1:1 ratio of reactants is used.[202]

The choice of initiator in radical additions of hydrogen sulfide to olefins is more critical than in thiol additions. Ultraviolet radiation was used initially, and it is still one of the best methods.[191] Hydrogen sulfide absorbs below about 2800 Å and is dissociated into hydrogen atoms and ·SH radicals by such radiation.[203] As in thiol-olefin additions, radiation of wavelength longer than 3000 Å can be used if a photosensitizer, such as acetone, tetraethyllead, or a mercury salt, is added. $\gamma$-Radiation[204] and x-rays[199a] have also been employed.

Peroxides are of limited usefulness as initiators, possibly because they enter into an oxidation-reduction reaction with hydrogen sulfide to produce sulfur, which is a good inhibitor of radical chain reactions. In studies with $n$-butyl vinyl ether, it was found that benzoyl peroxide, hydrogen peroxide, and the peroxides formed on long contact of the ether with air actually inhibit the radical addition and sometimes accelerate the ionic addition. The inhibition is probably to be ascribed to the formation of acidic substances.[196] On the other hand, ascaridole at 1% concentration initiated the addition smoothly. Ascaridole, however, did not initiate the addition of hydrogen sulfide to isopentyl vinyl ether.[197] Di-$t$-butyl peroxide has been reported to be effective for the reaction of diallyl ether with hydrogen sulfide to give polymer,[205] and, when combined with iron, an effective initiator for the addition to 2,5-dimethyl-2,4-hexadiene

[201] May, Ridgway, and Wadsworth, U.S. pat. 2,865,965 [C.A., 53, 10001 (1959)].
[202] Vaughan and Rust, U.S. pat. 2,522,589 [C.A., 45, 455 (1951)].
[203] Ramsay, J. Chem. Phys., 20, 1920 (1952).
[204] Dow Chemical Co., Brit. pat. 842,277 [C.A., 55, 5346 (1961)].
[205] McMillan, U.S. pat. 2,514,661 [C.A., 44, 9184 (1950)].

to give a mono- and a di-thiol.[193] Benzoyl peroxide has been used in the addition to di-n-butyl α-methyl-α'-methyleneadipate[206] Traces of oxygen initiate the addition of hydrogen sulfide to vinyl ethers[196] and vinyl sulfides,[179] but larger amounts (e g , 0 05% in the case of butyl vinyl ether) are inhibitory [196] Of all the radical initiators studied, azonitriles seem to be the most satisfactory for hydrogen sulfide additions.[190,193]

Ionic additions of hydrogen sulfide to olefinic hydrocarbons have been effected with many catalysts; e g , sulfur, sulfuric acid, Friedel-Crafts catalysts, alumina, metal sulfides and polysulfides, and silica. These reactions lead to products with normal (Markownikoff) orientation except that some high-temperature reactions catalyzed by metal sulfides furnish both normal and abnormal adducts [207] Ionic additions to α,β-unsaturated carbonyl compounds and nitriles have been catalyzed byalkoxides, amines, and sodium acetate, and the formation of α-mercaptoethyl ethers has been catalyzed by acids. Reviews of hydrogen sulfide additions to olefins have been given by Knunyants and Fokin[70] and Naylor.[194,208]

The x-ray-initiated reaction of hydrogen sulfide (in excess) with a series of mono- and disubstituted acetylenes led to the formation of vinyl thiols in addition to other products[208a]  For example, from propyne, both the *cis* and *trans* isomers of 1-propene-1-thiol were obtained along with 1,2-dimercaptopropane and polymeric oil  Similar results were obtained

$$CH_3C{\equiv}CH + H_2S \longrightarrow CH_3CH{=}CHSH + CH_2SHSCH_2SH$$
<center>(cis and trans)</center>
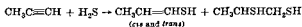
with 3,3,3-trifluoropropyne, 2-butyne, and hexafluoro-2-butyne, except that in the last mentioned case a single isomer of hexafluoro-2-butene-2-thiol (43a) was obtained  From phenylacetylene the major product

<center>

$$\underset{\textbf{43}a}{CF_3CH{=}CCF_3} \qquad \underset{\textbf{43}b}{(C_6H_5CH{=}CH)_2S}$$

</center>

was bis-(β-phenylvinyl)sulfide (43b).

**Experimental Conditions.** Ultraviolet-initiated reactions have been carried out by irradiating the reactants in a vessel cooled to −80° with the ultraviolet source immersed directly in the mixture,[192] or in sealed quartz tubes cooled in a transparent liquid in a quartz container with an external ultraviolet source [191]  Ultraviolet sources radiating at 2537 Å

[195] Bortnick and Fegley, French pat. 1,218,413 (1960).
[207] Barr and Keyes, Ind Eng. Chem , 26, 1111 (1934)
[208] Naylor, J. Polymer. Sci , 1, 305 (1946).
[208a] Stacey and Harris, J. Am Chem Soc , 85, 963 (1963).

(e.g., a Hanovia SC-2537 lamp) are generally used. The times vary from a few minutes, for 1-butene at 0°,[191] to several hours, for 1-chlorocyclohexene at —78°.[97] Temperatures ranging from —78° to room temperature have been used. Temperature effects have been noted. The addition of 1-butene at 0° proceeded in 89% conversion while at —78° the conversion was 40–45%.[191] Pyrex vessels can be used in experiments employing sensitizers (generally acetone) and ultraviolet sources radiating at or above 3000 Å. Additions to vinyl silanes have been accomplished by irradiating the refluxing silane while hydrogen sulfide was bubbled through.[209] Ultraviolet-initiated additions have been carried out in the gas phase, but they are much slower than in the liquid phase.

In azonitrile-initiated experiments, $\alpha,\alpha'$-azo-bis(isobutyronitrile,[190,200] 1,1'-azo-bis(cyclohexanecarbonitrile),[190] and $\alpha,\alpha'$-azo-bis($\alpha,\gamma$-dimethyl-maleonitrile)[190] in amounts varying from a few tenths of 1% to a few per cent have been used. Generally the reactants are sealed in glass[200] or metal[190] vessels without a solvent and are heated for a period of a few hours to 60 hours at catalyst decomposition temperatures. In peroxide-initiated experiments, ascaridole (1%),[196] di-$t$-butyl peroxide (5%),[205] and a peroxidized dioxane-hydrogen chloride solution[196] have been used, the procedures being analogous to those for azonitrile-initiated experiments. In the oxygen-initiated additions to vinyl ethers, the reactants containing 0.01% or less of oxygen are sealed in glass vessels and allowed to stand at room temperature for several days.[196]

## Addition of Bisulfite Ion to Olefins and Acetylenes*

Bisulfite ion in aqueous solution adds in the anti-Markownikoff sense to olefins and acetylenes in the presence of certain oxidants or free radical initiators. For example, from propylene and ammonium bisulfite in the presence of oxygen, ammonium $n$-propane-1-sulfonate is obtained.[210] The free radical chain mechanism for the olefin reaction, originally proposed

$$CH_3CH{=}CH_2 + NH_4HSO_3 \rightarrow CH_3CH_2CH_2SO_3NH_4$$
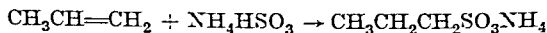
by Kharasch and co-workers,[211] may be formulated as follows.

$$HSO_3^- \xrightarrow{\text{Initiator}} \cdot SO_3^-$$

$$\cdot SO_3^- + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \longrightarrow \cdot \overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}SO_3^-$$
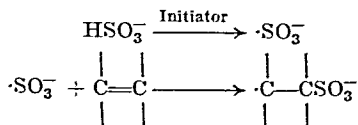
[209] Zappel, Ger. pat. 1,000,817 [$C.A.$, 53, 13054 (1959)].

* The addition of bisulfite to olefins has been reviewed by Walling (ref. 45, p. 326) and Mayo and Walling (ref. 8). A summary of the work done before the free radical nature of the reaction was recognized is given by Kharasch, May, and Mayo.[210]

[210] Kharasch, May, and Mayo, $J.\ Org.\ Chem.$, 3, 175 (1938).

[211] Kharasch, May, and Mayo, $Chem.\ \&\ Ind.$ ($London$), 57, 774 (1938).

$$\overset{|}{-}\overset{|}{C}-CSO_3^- + HSO_3^- \longrightarrow \overset{|}{C}H CHSO_3^- + SO_3^-$$
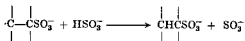
The exact nature of the adding species, represented here as the sulfite ion radical, is not known with certainty; it may well be the bisulfite radical, $HSO_3$.* In any event, the adding species does contain sulfur, since in those products whose structures have been determined the sulfur atom is attached to the carbon atom generally attacked by free radicals.

The reaction has not been studied much. No stereochemical studies have been made, and no information concerning the reversibility of the addition step has been obtained. Neither has its scope been clearly defined. For the bisulfite source, sodium, potassium, ammonium, and some amine[214] bisulfites have been employed. In the majority of examples reported, oxygen was the initiator, either added intentionally or adventitiously. Other oxidants or radical sources such as peroxides,[215] nitrite, and nitrate[210] have also been used. In oxygen-initiated additions there occurs a competing oxidation of bisulfite to bisulfate, a disadvantage not inherent in peroxide-initiated reactions.

Both terminal and internal[210,216] olefins undergo the reaction satisfactorily. With ethylene, either the 1:1 adduct[210,217] or low telomers[218] can be obtained, depending on the ethylene pressure employed. Peroxide-initiated bisulfite addition to fluoroolefins occurs readily, affording a route

$$CH_2{=}CH_2 + HSO_3^- \begin{array}{c} \xrightarrow{35\text{-}40\ p\,s\,i} C_2H_5SO_3^- \\ \xrightarrow{700\text{-}1000\ atm} H(CH_2CH_2)_nSO_3^- \\ {\scriptstyle [n\ =\ 4\ (average)]} \end{array}$$
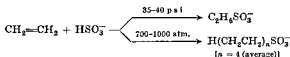
to highly fluorinated alkanesulfonic acids.[215] Other substituted olefins,

$$n\text{-}C_5F_{11}CF{=}CF_2 + NaHSO_3 \xrightarrow{Peroxide} n\text{-}C_6F_{11}CHFCF_2SO_3Na$$
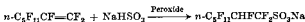
including vinyl chloride, allyl alcohol, styrene, vinyl sulfides, vinyl sulfoxides, and vinyl sulfones, also undergo the reaction.

* Both the sulfite ion radical and the bisulfite radical have been proposed as intermediates in the autoxidation of bisulfite ion and sulfite ion by oxygen.[212,213]

[212] Bäckstrom, *Z. Physik Chem*, **B25**, 122 (1934).

[213] Franck and Haber, *Sitzber Preuss Akad Wiss. Physik Math Kl*, p 250 (1931) [*C.A.*, **25**, 4773 (1931)].

[214] Kharasch, Schenck, and Mayo, *J Am. Chem. Soc*, **61**, 3092 (1939).

[215] Koshar, Trott, and LaZerte, *J. Am Chem. Soc*, **75**, 4595 (1953).

[216] Böhme Fettchemie, Brit. pat., 756,105 [*C.A.*, **51**, 7366 (1957)].

[217] Kolker and Lapworth, *J. Chem. Soc*, **127**, 307 (1925).

[218] Hanford, U S pat. 2,398,426 [*C.A.*, **40**, 3828 (1946)].

Hydroxyl-substituted olefins, e.g., allyl carbinol,[216] work particularly well, probably because of their relatively high solubility in the aqueous bisulfite solution.

$$\text{HOCH}_2\text{CH}_2\text{CH}{=}\text{CH}_2 + \text{NaHSO}_3 \xrightarrow{\text{O}_2} \text{HO(CH}_2)_4\text{SO}_3\text{Na}$$
$$\text{(almost quantitative)}$$
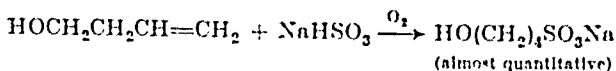
In the oxygen-catalyzed addition of bisulfite ion to allyl alcohol the sole product at $p$H 7 is the 1:1 adduct 44, but at $p$H 4 a sulfonate-sulfinate 45 is virtually the exclusive product.[219-221] A possible mechanism for the

$$\text{KHSO}_3 + \text{HOCH}_2\text{CH}{=}\text{CH}_2 \xrightarrow{\text{O}_2} \text{HOCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{K} + \underset{\underset{44}{\underset{\text{KO}_2\text{S}\quad\text{SO}_3\text{K}}{|\quad\;|}}}{\text{HOCH}_2\text{CHCH}_2}$$

$$44 \qquad\qquad 45$$
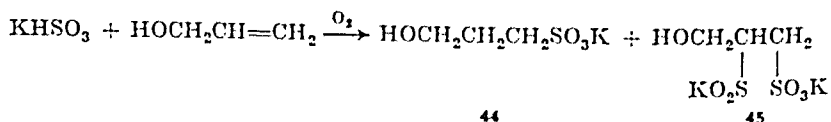
formation of 45 is the reaction of the intermediate radical 46 with sulfur dioxide followed by chain transfer with bisulfite ion.

$$\underset{\underset{46}{\underset{\text{SO}_3\text{K}}{|}}}{\text{HOCH}_2\dot{\text{C}}\text{HCH}_2} + \text{SO}_2 \longrightarrow \underset{\underset{\cdot\text{O}_2\text{S}\quad\text{SO}_3\text{K}}{|\quad\;|}}{\text{HOCH}_2\text{CHCH}_2} \xrightarrow{\text{HSO}_3^-} \underset{\underset{\text{HO}_2\text{S}\quad\text{SO}_3\text{K}}{|\quad\;|}}{\text{HOCH}_2\text{CHCH}_2}$$
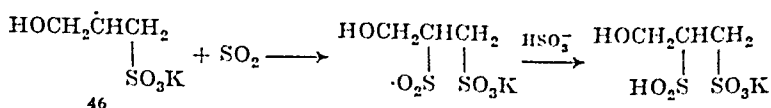
In oxygen-catalyzed addition of bisulfite ion to styrene, two products in addition to the 1:1 adduct 48 are obtained.[214] They are 2-hydroxy-2-phenylethanesulfonic acid (49), the major product of the reaction, and 2-phenylethylenesulfonic acid (50). The three products are not interconvertible under the reaction conditions and presumably arise from the same intermediate radical, the two new products deriving from reactions of this radical with oxygen.

$$\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2 + \text{NaHSO}_3 \rightarrow \text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{SO}_3\text{Na} \xrightarrow{\text{HSO}_3^-} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$$
$$47 \qquad\qquad 48$$

$$\overset{\text{OH}}{\underset{49\ (65\%)}{\overset{|}{\text{C}_6\text{H}_5\text{CHCH}_2\text{SO}_3\text{Na}}}} \xleftarrow{\text{OH}^-} \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{HCH}_2\text{SO}_3\text{Na} \qquad \underset{50\ (10\%)}{\text{C}_6\text{H}_5\text{CH}{=}\text{CHSO}_3\text{Na}} + \dot{\text{O}}\text{OH}$$
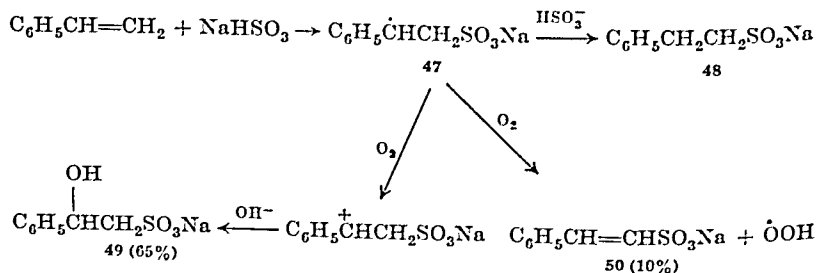
If the oxygen is replaced by nitrite or persulfate, none of the unsaturated sulfonate 50 is formed, presumably because of the inability of these oxidants to remove a hydrogen atom from the intermediate radical 47.

[219] Helberger, *Angew. Chem.*, **73**, 69 (1961).
[220] Helberger, Ger. pat. 915,693 [*C.A.*, **49**, 10357 (1955)].
[221] Helberger, *Ann.*, **588**, 71 (1954).

It has been shown conclusively that with ordinary olefins no addition of bisulfite occurs in the absence of an oxidant or other radical-producing source.[220] On the other hand, bisulfite ion adds very rapidly to $\alpha,\beta$-unsaturated carbonyl compounds and nitriles. Since this reaction is completely unaffected by factors which usually promote or retard radical addition, it is obviously ionic in nature.[222,223]

$$SO_3^{-2} + CH_2\!=\!CHCO_2CH_3 \rightarrow {}^-O_3SCH_2CHCO_2CH_3 \xrightarrow{H_2O} {}^-O_3SCH_2CH_2CO_2CH_3$$
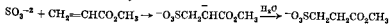
In the addition of bisulfite ion to acetylenes, both 1:1 and 2:1 adducts are formed.[224] 1-Hexyne yields sodium n-1-hexene-1-sulfonate and disodium hexane-1,2-disulfonate. Similarly, from phenylacetylene, both adducts are obtained    The 2:1 adduct is apparently exclusively

$$n\text{-}C_4H_9C\!\equiv\!CH + NaHSO_3 \xrightarrow{O_2}$$
$$n\text{-}C_4H_9CH\!=\!CHSO_3Na + n\text{-}C_4H_9CH(SO_3Na)CH_2SO_3Na$$
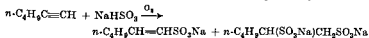
disodium 1-phenylethane-1,2-disulfonate 51 in contrast to the diadducts

$$C_6H_5C\!\equiv\!CH + NaHSO_3 \rightarrow C_6H_5CH\!=\!CHSO_3Na \rightarrow$$
$$C_6H_5CH(SO_3Na)CH_2SO_3Na$$
$$\mathbf{51}$$
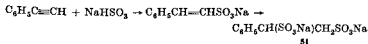
from the radical addition of thiols to phenylacetylene in which both thiyl groups are terminal.[170]

**Experimental Conditions.** Most radical additions of bisulfite ion to olefins and acetylenes have been carried out in aqueous (20-40%) buffered solutions containing an excess of bisulfite with oxygen as the initiator. Many reactions have been carried out at the boiling point with air or oxygen passed through the reaction mixture.[225,226] Pressure vessels have been used for reactions involving gaseous olefins.

Since oxygen is consumed in the competing autoxidation of bisulfite to bisulfate, a continuous supply of oxygen is necessary to achieve high conversions    The relative amounts of the two products, i.e., bisulfite ion and the addition product, depend largely on the nature of the olefin, its solubility in the reaction mixture, and the ease with which addition takes place. There is an optimum pH (5–7) for the addition reaction; this value varies somewhat with the olefin used and with the cation initially associated with the bisulfite ion employed    Since the autoxidation of bisulfite ion results in an increase in acidity (bisulfate is more acidic than bisulfite),

[222] Schenck and Danishefsky, J Org Chem , **16**, 1683 (1951).

[223] Morton and Landfield, J Am Chem Soc , **74**, 3523 (1952)

[224] W J Wemsch, Doctoral Dissertation, New York University, 1955, Dissertation Abstr , **15**, 668 (1956)

[225] I. G Farbenindustrie, Brit. pat  454,675 [C A., 31, 1430 (1937)]

[226] Ufer, Ger. pat  681,338 [C A , 36, 2052 (1942)]

a disadvantageous effect of the concurrent autoxidation is a change in the $pH$ from the optimum, which slows down the addition. This effect can be offset by buffering with sulfite ion, which is oxidized to sulfate ion. Buffering is accomplished by the addition of ammonia when ammonium bisulfite is used as the bisulfite source.[210]

With radical initiators other than oxygen, e.g., benzoyl peroxide, $t$-butyl perbenzoate, and 2,2-bis($t$-butylperoxy)butane, particularly in solvent systems such as aqueous methanol, aqueous hexanolamine, and aqueous pyridine, yields of alkanesulfonic acid salts in the range 80–100% have been obtained in autoclave reactions.[227] Similarly, the peroxide-initiated addition to fluoroölefins in aqueous borax solution occurs with relatively high yields in autoclaves.[215]

The temperatures employed in experiments with peroxide catalysts are generally those required for decomposition of the catalyst. With oxygen, temperatures between −5° and 100° have been used, room temperature being most common.

### Addition of Sulfonyl and Sulfuryl Halides to Olefins

Free radical chain addition to olefins of a variety of compounds containing sulfonyl halide groups, e.g., sulfuryl chloride, sulfuryl chloride fluoride, aromatic sulfonyl halides, and N-chlorosulfonylphthalimide, have been reported.

$$RSO_2X + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \rightarrow RSO_2\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$
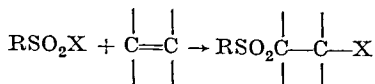
The additions of arylsulfonyl halides to give $\beta$-haloalkyl aryl sulfones have

$$C_6H_5SO_2Cl + CH_2{=}C(CH_3)_2 \rightarrow C_6H_5SO_2CH_2CCl(CH_3)_2$$
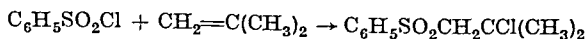
received the most attention, and a typical radical chain mechanism has been proposed.

$$ArSO_2X \rightarrow ArSO_2\cdot$$
$$52$$

$$ArSO_2\cdot + CH_2{=}CHR \rightarrow ArSO_2CH_2\dot{C}HR$$

$$ArSO_2CH_2\dot{C}HR + ArSO_2X \rightarrow ArSO_2CH_2CHXR + ArSO_2\cdot$$

$$ArSO_2CH_2\dot{C}HR + CH_2{=}CHR \rightarrow ArSO_2CH_2CH(R)CH_2\dot{C}HR$$
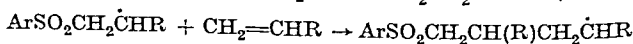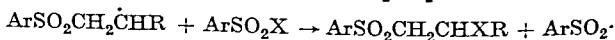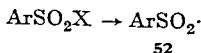
The arylsulfonyl radical 52 is the adding or chain-carrying species since, in all products whose structures have been determined, the sulfonyl group is attached to the carbon atom generally attacked by radicals. Arylsulfonyl chlorides, bromides, and iodides all undergo the reaction.

[227] Harman, U.S. pat. 2,504,411 [*C.A.*, 44, 5897 (1950)].

In a study of comparative reactivities of benzenesulfonyl halides and bromotrichloromethane in additions to olefins, the following order was determined.[229] p-Chlorobenzenesulfonyl chloride has been reported to

$$C_6H_5SO_2I > C_6H_5SO_2Br > BrCCl_3 > C_6H_5SO_2Cl$$
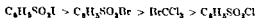
be considerably more reactive than benzenesulfonyl chloride.[229]

Both internal and terminal olefins undergo the reaction readily. With ethylene, p-chlorobenzenesulfonyl chloride forms a series of telomers in addition to the 1:1 adduct.[229] Substituted olefins, e.g., allyl acetate, methyl acrylate, vinyl bromide, methyl methacrylate, allyl chloride, acrylonitrile, styrene, and 3,3-diacetoxy-1-propene react, and the products obtained are those expected if it is assumed that $ArSO_2$· is the adding species.

The stereochemistry of arylsulfonyl halide additions has received some attention  Ultraviolet-catalyzed addition of benzenesulfonyl iodide to either cis- or trans-2-butene yields the same mixture of diastereomeric addition products under conditions in which the individual olefins are not isomerized.[230,231] Thus, in a fashion analogous to radical thiol additions, equilibration of the intermediate radical occurs before the transfer step takes place.
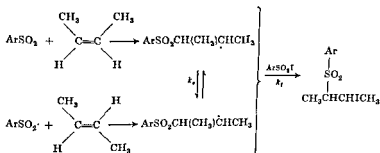


The value of $(k_t/k_c)[C_6H_5SO_2I]$ has been estimated as $\geq 10^4$ in this case.[230]

Peroxide- or ultraviolet-initiated addition of p-toluenesulfonyl chloride to norbornene occurs trans, apparently exclusively, giving exo-2-p-toluenesulfonyl-endo-3-chloronorbornane(53) without rearrangement.[149,232]

[229] J. H. McNamara, Doctoral Dissertation, Pennsylvania State University, 1956, Dissertation Abstr., 17, 226 (1957).
[230] Ladd, U S. pat. 2,573,580 [C A , 46, 7588 (1952)].
[231] Skell, Woodworth, and McNamara, J. Am Chem Soc , 79, 1253 (1957)
[232] Skell and McNamara, J. Am. Chem. Soc , 79, 85 (1957).
[233] Cristol and Reeder, J. Org Chem., 26, 2182 (1961).

This result is unusual in that radical additions to norbornene generally occur *cis*. Evidently approach of *p*-toluenesulfonyl chloride on the *exo* side of the intermediate radical for transfer is impossible for steric



**53**
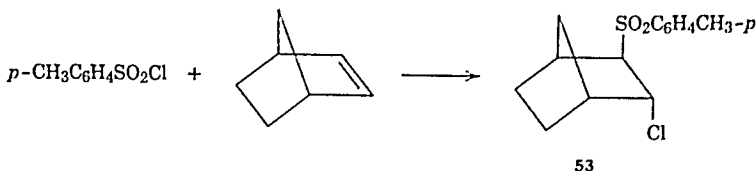
reasons. Similarly, *trans* addition to *endo-exo*-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (54) without rearrangement was noted.[149,232] The addition to norbornadiene occurs with rearrangement to give 3-*p*-toluenesulfonyl-5-chloronortricyclene.[149,232]



**54**
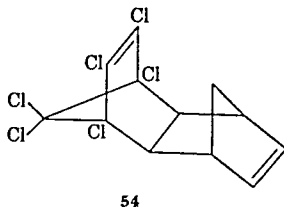
Peroxide-initiated reaction of trichloromethanesulfonyl chloride with styrene leads to addition of the elements of carbon tetrachloride with loss

$$Cl_3CSO_2Cl + C_6H_5CH=CH_2 \xrightarrow{\text{Peroxide}} C_6H_5CHClCH_2CCl_3 + SO_2$$
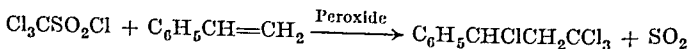
of sulfur dioxide.[233] There are apparently no examples of radical additions of alkanesulfonyl halides to olefins.

Peroxide- or ultraviolet-initiated addition of sulfuryl fluoride chloride to olefins results in the formation of chloroalkanesulfonyl fluorides, by a radical chain process.[234,235]

$$ClSO_2F \xrightarrow{\text{Initiator}} \cdot SO_2F$$

$$RCH=CH_2 + \cdot SO_2F \longrightarrow R\dot{C}HCH_2SO_2F$$

$$R\dot{C}HCH_2SO_2F + ClSO_2F \longrightarrow RCHClCH_2SO_2F + \cdot SO_2F$$
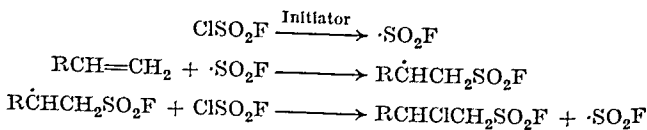
There is little or no cleavage of the sulfur-fluorine bond. Yields with long-chain terminal olefins, e.g., 1-octadecene, are high; with olefins of low molecular weight, telomers containing 2 and 3 olefin units are obtained

[233] Ladd and Kiley, U.S. pat. 2,606,213 [*C.A.*, **47**, 6440 (1953)].
[234] Tiers, Fr. pat. 1,170,791; U.S. pat. 2,846,472 [*C.A.*, **53**, 12175 (1959)].
[235] Tiers, Fr. pat. 1,170,792; U.S. 2,846,472 [*C.A.*, **53**, 12175 (1959)].

in addition to the 1:1 adduct. With fluorinated olefins, chloro-polyfluoroalkanesulfonyl fluorides containing an average of 4 to 18 olefin units are formed

The reactions of sulfuryl chloride with terminal olefins in the presence of sulfur dioxide result in the formation of sulfones in 15–30% yields, and of dichloroalkanes in 50–80% yields. One-to-one adducts (sulfonyl chlorides) have not been obtained in these reactions

$$n\text{-}C_6H_{13}CH=CH_2 + SO_2Cl_2 \rightarrow (n\text{-}C_6H_{13}CHClCH_2)_2SO_2 + n\text{-}C_6H_{13}CHClCH_2Cl$$
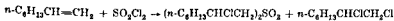
Two mechanisms have been proposed by Kharasch and Zavist [236],[237] The first, a typical chain type involving the intermediate formation of

$$SO_2Cl_2 \xrightarrow{\text{Initiator}} SO_2Cl$$

$$\cdot SO_2Cl + RCH=CH_2 \longrightarrow RCHClCH_2SO_2Cl$$

$$RCHClCH_2SO_2Cl + SO_2Cl_2 \longrightarrow RCHClCH_2SO_2Cl + SO_2Cl$$

$$RCHClCH_2SO_2Cl \xrightarrow{\text{Initiator}} RCHClCH_2SO_2$$

$$RCHClCH_2SO_2 + RCH=CH_2 \longrightarrow RCHClCH_2SO_2CH_2\dot{C}HR$$

$$RCHClCH_2SO_2CH_2CHR + SO_2Cl_2 \longrightarrow (RCHClCH_2)_2SO_2 + SO_2Cl$$
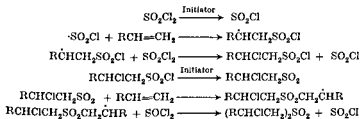
sulfonyl chloride which adds to the olefin by a subsequent chain reaction, is unlikely since it was found that an alkanesulfonyl chloride would not add to the olefin under conditions in which sulfones are formed. The second scheme postulates a rearrangement of the intermediate radical 55

$$\underset{\mathbf{55}}{R\dot{C}HCH_2SO_2} \xrightarrow{\text{Rearrangement}} RCHClCH_2SO_2$$

$$RCHClCH_2SO_2 + RCH=CH_2 \longrightarrow RCHClCH_2SO_2CH_2\dot{C}HR$$

$$RCHClCH_2SO_2CH_2\dot{C}HR + SO_2Cl_2 \longrightarrow (RCHClCH_2)_2SO_2 + SO_2Cl$$
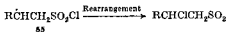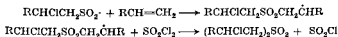
with a shift of chlorine from sulfur to the β-carbon atom and thus obviates the necessity for an alkanesulfonyl chlorine-olefin addition. At the present time this mechanism seems the more likely, but further work is necessary to substantiate it.

The only unequivocal example of the formation of an alkanesulfonyl chloride by a radical process from an olefin and sulfuryl chloride is the telomerization of ethylene with sulfuryl chloride.[238] A radical mechanism

$$CH_2=CH_2 + SO_2Cl_2 \xrightarrow{\text{Peroxide}} Cl(CH_2CH_2)_nSO_2Cl$$
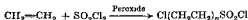
has been postulated for the formation of β,β-dichloroethanesulfonyl

[236] Kharasch and Zavist, J. Am. Chem. Soc , 73, 964 (1951)
[237] Kharasch and Zavist, J. Am Chem Soc , 73, 3826 (1948)
[238] Hanford and Joyce, U S patent. 2,440,800 [C A , 42, 6372 (1948)]

chloride from a reaction of vinyl chloride and sulfuryl chloride catalyzed by sulfur chlorides,[236,239] but it seems unlikely that this can be a radical reaction.

Mixtures of N-chlorosulfonylphthalimide (56) and 1-decene or 1-octene react in the presence of peroxide to give N-(chloroalkylsulfonyl)phthalimides, presumably by a chain mechanism analogous to that written for



56

$(R = n\text{-}C_6H_{13}, n\text{-}C_8H_{17})$
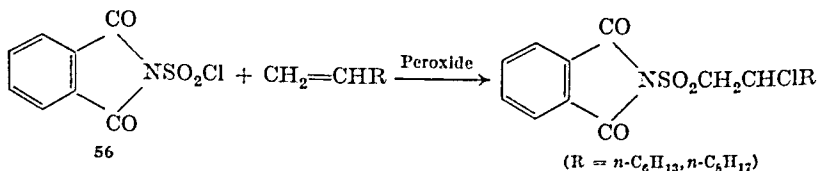
aromatic sulfonyl halide additions.[240] Efforts to effect additions of N-chlorosulfonylphthalimide to styrene, indene, vinyl acetate, or allyl chloride, and of N,N-dimethylsulfamyl chloride and N,N-dimethylcarbamyl chloride to 1-octene, failed.

**Experimental Conditions.** The additions of aromatic sulfonyl halides and sulfuryl chloride fluoride have been carried out by heating the reactants (in an autoclave if the olefin is low-boiling), at the decomposition temperature of the azonitrile or peroxide catalyst.[229,235,241] Benzenesulfonyl iodide additions have been accomplished by ultraviolet irradiation of the olefin and the freshly prepared iodide in carbon tetrachloride solution.[228,231] The additions of sulfuryl chloride to terminal olefins to give sulfones have been carried out by adding a solution of sulfuryl chloride in the olefin to a suspension of benzoyl peroxide in the olefin at 60–65° through which a slow stream of sulfur dioxide is passing. Reaction times are 6–7 hours.[236,237]

### Miscellaneous Additions to Form C—S Bonds

**Addition of Sulfenyl Chlorides.** Sulfenyl chlorides, which undergo ionic addition to hydrocarbon olefins readily,[242] have recently been shown to undergo free radical additions also.[243–245] Thus trichloromethanesulfenyl chloride has been reported to add to styrene under the influence of benzoyl peroxide or ultraviolet radiation.[243,244] The product isolated

[239] Yakubovich and Zinov'ev, *J. Gen. Chem. USSR*, **17**, 2028 (1947) [*C.A.*, **43**, 1248 (1949)].
[240] Kharasch and Mosher, *J. Org. Chem.*, **17**, 453 (1952).
[241] Ladd, U.S. pat. 2,521,068 [*C.A.*, **45**, 653 (1951)].
[242] Kharasch, Buess, and Strashun, *J. Am. Chem. Soc.*, **74**, 3422 (1952).
[243] Prey, Gutschik, and Berbalk, *Monatsh. Chem.*, **91**, 794 (1960).
[244] Prey and Gutschik, *Monatsh. Chem.*, **90**, 551 (1959).
[245] Harris, *J. Am. Chem. Soc.*, **84**, 3148 (1962).

was assigned structure 57, with the chlorine atom on the terminal carbon

$$Cl_2CSCl + C_6H_5CH=CH_2 \rightarrow C_6H_5CH(SCCl_3)CH_2Cl$$

<div align="center">57</div>
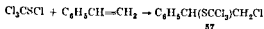
atom indicating that a chlorine atom, rather than the trichloromethylthiyl radical, is the adding species. A chain mechanism has been proposed [243]

$$Cl_2CSCl \rightarrow Cl_2CS + Cl$$

$$C_6H_5CH=CH_2 + Cl \rightarrow C_6H_5CHClCH_2Cl$$

$$C_6H_5\dot{C}HCH_2Cl + Cl_2CSCl \rightarrow C_6H_5CH(SCCl_3)CH_2Cl + Cl\cdot$$

<div align="center">57</div>
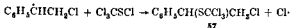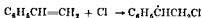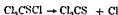
The ultraviolet- or azonitrile-initiated reaction of trifluoromethane-sulfenyl chloride with several unsymmetrical fluoroolefins has yielded both possible 1:1 adducts.[245] For example, from the reaction with trifluoroethylene, both 58 and 59 were obtained. In previously studied radical additions of trifluoromethanethiol, hydrogen bromide, and trifluoromethyl iodide to trifluoroethylene, two 1:1 adducts have also

$$CF_3SCl + CHF=CF_2 \xrightarrow{\text{UV}} CF_3SCF_2CHFCl + CF_3SCHFCF_2Cl$$

<div align="center">58 (82%)    59 (18%)</div>
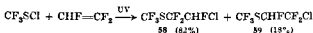
been obtained. The predominant isomer results from attack by the chain-carrying radical on the monofluorinated carbon atom. Thus, in the addition of trifluoromethanethiol, 60 is the predominant product  Since the orientation with respect to the CF₃S group of the predominant adduct

$$CF_3SH + CHF=CF_2 \xrightarrow{\text{UV}} CF_3SCHFCHF_2 + CF_3SCF_2CH_2F$$

<div align="center">60 (98%)    61 (2%)</div>
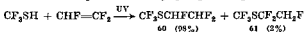
(58) obtained in the sulfenyl chloride reaction is just opposite to that (60) obtained in the corresponding thiol addition, it appears that in this case also the predominant adding species must be chlorine atom Several other examples of trifluoromethanesulfenyl chloride additions have been studied and, when a direct comparison with the analogous tri-fluoromethanethiol addition was made, it was found that the orientation with respect to the trifluoromethylthio group was reversed (Table VIII)

<div align="center">TABLE VIII</div>

<div align="center">COMPARISON OF COMPOSITION OF 1:1 ADDUCT FRACTIONS FROM CF₃SCl AND</div>
<div align="center">CF₃SH RADICAL ADDITIONS</div>

The numbers represent the % composition of the 1:1 adduct fraction with respect to the orientation of the CF₃S group.

| | CH₂=CHCl | | CF₂=CHF | | CF₂=CFCl | | CF₂=CH₂ | |
|---|---|---|---|---|---|---|---|---|
| CF₃SCl | 5 | 95 | 82 | 18 | 25 | 75 | 78 | 22 |
| CF₃SH | 100 | 0 | 2 | 98 | 100 | 0 | 0 | 100 |

Since in each of the sulfenyl chloride additions both 1:1 adducts are obtained, it appears that the reaction is also occurring, to some extent at least, by a mechanism analogous to the thiol mechanism involving the $CF_3S$ radical as the chain-carrying species.

$$CF_3SCl \xrightarrow{UV} CF_3S\cdot + Cl\cdot$$

$$CF_3S\cdot + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C} } \longrightarrow CF_3S\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

$$CF_3S\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + CF_3SCl \longrightarrow CF_3S\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Cl + CF_3S\cdot$$
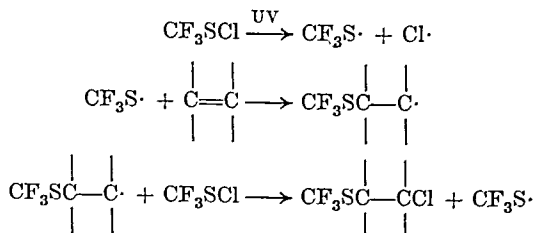
Ultraviolet- or peroxide-initiated additions of trichloromethanesulfenyl chloride to cyclohexene,[243,244] 1-hexene,[243] 1-octene,[243] allyl acetate,[243] allyl chloride,[243] indene,[244] benzofuran,[244] and hexachlorodihydrothiophene[244] have also been carried out, but no pertinent structural data on the products have been reported.

**Addition of Sulfur Chloride Pentafluoride.** Recently radical additions of sulfur chloride pentafluoride ($SF_5Cl$) to olefins and acetylenes have been reported and a radical chain mechanism has been proposed.[246–249]

$$SF_5Cl \xrightarrow{Initiator} SF_5\cdot$$

$$SF_5\cdot + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow SF_5\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

$$SF_5\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow SF_5(\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}})_2\cdot \quad \text{etc.}$$

$$SF_5\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + SF_5Cl \longrightarrow SF_5\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Cl + SF_5\cdot$$
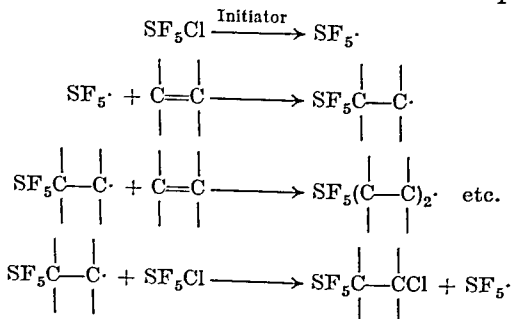
The ultraviolet-initiated addition to propylene yields 2-chloropropyl sulfur pentafluoride, indicating that the $SF_5$ radical is the adding species.

$$SF_5Cl + CH_3CH{=}CH_2 \xrightarrow{UV} CH_3CHClCH_2SF_5$$
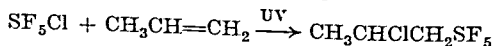
The orientation of the 1:1 adducts in additions to chlorotrifluoroethylene and trifluoroethylene also support this contention.

$$SF_5Cl + CHF{=}CF_2 \rightarrow SF_5CHFCF_2Cl$$

$$SF_5Cl + CFCl{=}CF_2 \rightarrow SF_5CF_2CFCl_2$$
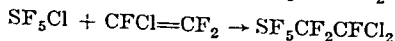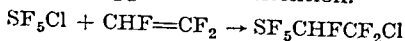
[246] Case, Ray, and Roberts, *Proc. Chem. Soc.*, **1960**, 401.
[247] Roberts, *Quart. Rev. (London)*, **15**, 40 (1961).
[248] Case, Ray, and Roberts, *J. Chem. Soc.*, **1961**, 2066.
[249] Case, Ray, and Roberts, *J. Chem. Soc.*, **1961**, 2070.

With tetrafluoroethylene in the presence of a free radical initiator, a series of telomers 62 is formed. When the reaction is initiated with ultraviolet radiation, a second series of telomers 63 is formed in addition

$$SF_5(CF_2CF_2)_nCl \qquad Cl(CF_2CF_2)_nCl$$
$$\phantom{SF_5(CF_2CF_2)_n}62 \qquad\qquad \phantom{Cl(CF_2CF_2)_n}63$$

to the series 62 Additions to ethylene, butadiene, and cyclohexene have also been carried out Isobutylene and styrene polymerize in the presence of sulfur chloride pentafluoride and apparently do not yield 1:1 adducts Additions with methyl acetylene give only 1:1 adducts

$$CH \equiv CH + SF_5Cl \rightarrow ClCH = CHSF_5$$
$$CH_3C \equiv CH + SF_5Cl \rightarrow CH_3CHCl = CHSF_5$$
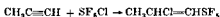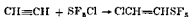
## Addition of Disulfides. *Organic Disulfides.*

Organic disulfides have been examined extensively as chain transfer agents in free radical vinyl polymerizations, and studies of the polymerization of styrene in the presence of disulfides have shown that the polymers contain $n$ RS groups per molecule (ref. 45, pp. 156–157, 332–333)

$$RSSR \rightarrow 2RS$$

$$RS \cdot + CH_2 = CHC_6H_5 \rightarrow RSCH_2\dot{C}HC_6H_5$$

$$RSCH_2\dot{C}HC_6H_5 + (x-1)C_6H_5CH = CH_2 \rightarrow RS[CH_2CH(C_6H_5)]_x$$

$$RS[CH_2CH(C_6H_5)]_x + RSSR \rightarrow RS[CH_2CH(C_6H_5)]_xSR + RS \cdot$$
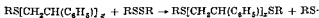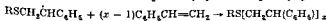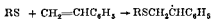
The magnitudes of disulfide-olefin transfer constants indicate that 1:1 chain addition of the more reactive disulfides to olefins should be possible Apparently, the only such reaction reported is the photoinitiated addition of $n$-butyl disulfide to vinyl acetate to give 1,2-bis($n$-butylthio)ethyl acetate (64)[76] It is not known whether this product is formed by a chain-propagating displacement step or by the addition of two RS radicals

$$CH_3CO_2CH = CH_2 + (n\text{-}C_4H_9)_2S_2 \rightarrow CH_3CO_2CHCH_2SC_4H_9\text{-}n$$
$$\phantom{CH_3CO_2CH = CH_2 + (n\text{-}C_4H_9)_2S_2 \rightarrow CH_3CO_2CHCH_2}SC_4H_9\text{-}n$$
$$\phantom{CH_3CO_2CH = CH_2 + (n\text{-}C_4H_9)_2S_2 \rightarrow } 64 \;(30\%)$$
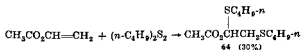
produced by photolysis of the disulfide Disulfide-olefin additions catalyzed by iodine have been reported, but these are ionic in nature[258 255 251a]

*Thiocyanogen.* Although a large number of additions of thiocyanogen to carbon-carbon double and triple bonds have been recorded[252] and

[253] Holmberg, *Arkiv Kemi Mineral. Geol.*, **12B**, No 14 (1939)

[252] Schneider and Bagnell *J. Org Chem*, **26**, 1984 (1961).

[251a] Schneider, Bagnell, and Murdoch, *J. Org Chem*, **26**, 1987 (1961)

[76] Wood, in Adams, *Organic Reactions*, Vol 3, Chap. 6, John Wiley & Sons, New York, 1946

although it has been noted that the reactions are accelerated by ultraviolet radiation, there has been very little study of the mechanism of the reaction. Quite recently, it was reported that the reaction is also influenced by the presence of peroxides, and a free radical mechanism was proposed.[253] Addition to the double bond to give **65** may be accompanied by allylic substitution to give **66**. The relative amounts of addition and substitution depend on the structure of the olefin. Cyclo-



hexene undergoes both addition and substitution, whereas 1-methyl-cyclohexene undergoes largely substitution and 1-octene exclusively addition. In view of the scanty literature on the free radical nature of thiocyanogen additions, and the fact that there is available a tabulation of many examples,[252] no further review will be presented in this chapter.
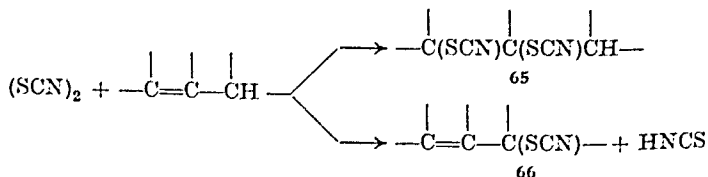
*Hydrogen Disulfide.* The decomposition of hydrogen disulfide in the presence of an excess of an olefin results in the formation of monosulfides, disulfides, and tetrasulfides. For example, from 1-pentene at 50°, diamyl monosulfide, diamyl disulfide, and diamyl tetrasulfide were obtained in yields of 31%, 12%, and 25%, respectively.[251,255]

$$CH_2=CHC_3H_7\text{-}n + H_2S_2 \rightarrow (n\text{-}C_5H_{11})_2S_n + H_2S$$
$$(n = 1, 2, 4)$$
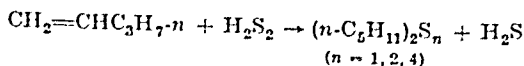
The decomposition of hydrogen disulfide to sulfur and hydrogen sulfide is a competing reaction and becomes of major importance with less reactive olefins. Thus the yield of hydrogen sulfide increased from 4–5% with 1-pentene to 21% with 2-pentene, and to 30% with cyclohexene. Other olefins which have been tried in this reaction, but for which products have not been disclosed, include styrene, isoprene, and α-methylstyrene.

A chain mechanism with an initiation step involving scission of the S—S bond of hydrogen disulfide has been proposed to account for the products formed.[255] However, the structures of the products have

apparently not been determined, and more research is necessary to establish that the reactions proceed by way of a free radical mechanism

## ADDITION OF SILANES TO OLEFINS AND ACETYLENES

The synthesis of organosilicon compounds by adding to olefins silanes containing one or more Si—H bonds was first reported in 1947 by three groups of investigators Sommer, Pietrusza, and Whitmore[256] and Burkhard and Krieble[257] reported independent studies of the peroxide-initiated additions of trichlorosilane. The former group also noted the ultraviolet-initiated addition of trichlorosilane to 1-octene, and the latter workers included methyldichlorosilane and a rather wide variety of unsaturates in their study. The third paper, by Barry, DePree, Gilkey, and Hook,[258] reported the thermal, uncatalyzed addition of silanes to olefins under pressure. Subsequently a substantial amount of research on the radical addition of silanes to unsaturates appeared in published papers and in the patent literature Concurrently, ionic additions, catalyzed by metals and metal salts (e.g., platinum and potassium chloroplatinate) have been found and explored extensively

This discussion and the accompanying tables are concerned only with the free radical reactions. The metal and metal salt-catalyzed reactions, which are the subject of a considerable body of literature, are excluded. A recent report states that iron pentacarbonyl catalyzes the free radical addition of silanes to olefins Although there is room for doubt concerning the mechanism of reaction with this catalyst, examples are included in the tables.

### Mechanism; Scope and Limitations

The free radical chain addition of silanes to olefins and acetylenes occurs only with compounds having one or more hydrogen atoms attached to silicon. This fact and its corollary, the failure to observe additions involving Si—X bonds (X = Cl or Br), can be accounted for by the energetics of the respective displacement steps[45]

$$H_3SiCH_2CH_2\cdot + SiH_4 \rightarrow H_3SiCH_2CH_3 + \cdot SiH_3 \qquad \Delta H = -14 \text{ kcal/mole}$$

$$Cl_3SiCH_2CH_2\cdot + SiCl_4 \rightarrow Cl_3SiCH_2CH_2Cl + \cdot SiCl_3 \qquad \Delta H = +17 \text{ kcal/mole}$$
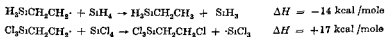
The mechanism of the reaction is illustrated by the addition of trichloro-silane to ethylene

[256] Sommer, Pietrusza, and Whitmore, J. Am. Chem. Soc., 69, 188 (1947).

[257] Burkhard and Krieble, J. Am. Chem. Soc., 69, 2687 (1947).

[258] Barry, DePree, Gilkey, and Hook, J. Am. Chem. Soc., 69, 2916 (1947).

$$HSiCl_3 \xrightarrow{\text{Initiation}} H\cdot + \cdot SiCl_3$$
$$\cdot SiCl_3 + CH_2{=}CH_2 \longrightarrow Cl_3SiCH_2CH_2\cdot$$
$$Cl_3SiCH_2CH_2\cdot + HSiCl_3 \longrightarrow Cl_3SiCH_2CH_3 + \cdot SiCl_3$$
$$Cl_3SiCH_2CH_2\cdot + CH_2{=}CH_2 \longrightarrow Cl_3SiCH_2CH_2CH_2CH_2\cdot \quad \text{etc.}$$
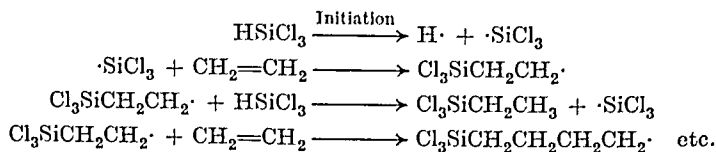
The formulation of the initiation step depends, of course, on the nature of the initiator. Radiation or thermal initiation probably proceeds as shown. With peroxides or other chemical initiators, initiation should probably be written to indicate abstraction of the hydrogen atom from trichlorosilane by an initiator fragment.

Addition has been initiated in a variety of ways, including exposure to ultraviolet[256,259] or ionizing radiation,[260] heating at 160–400° in the absence of any added catalyst,[258] and heating in the presence of peroxides[256,257] or azo compounds.[261,262] The peroxides used most frequently as initiators are acetyl peroxide, t-butyl perbenzoate, di-t-butyl peroxide, and, especially, benzoyl peroxide. A study has been made of the influence of a wide variety of substances on the t-butyl perbenzoate-catalyzed addition of trichlorosilane to 1-pentene.[263] Tin promotes the reaction, apparently through an induced decomposition of the peroxide, and with a mixture of tin and stannic chloride the reaction is violent even at room temperature. Such substances as alcohol, nickel, lead, zinc, traces of water and silicone grease are without significant effect, while iron and iron salts are very effective inhibitors. It has recently been reported that iron pentacarbonyl is an effective initiator for the reaction.[264] The formation of additive dimers ($R_3SiCH_2CHRCHRCH_2SiR_3$) is suggestive of the free radical character of the iron pentacarbonyl-initiated reaction.

Ultraviolet radiation is a generally effective and often very convenient initiator. Peroxides appear to give higher yields of adduct, but in the addition of trichlorosilane to 2-methyl-2-butene the higher yield is obtained with ultraviolet radiation.[259] Triphenylsilane adds to 1-octene in the presence of benzoyl peroxide but not under ultraviolet irradiation.[265] In the additions of trichlorosilane and of methyldichlorosilane to a number of fluorinated olefins, higher yields were obtained with di-t-butyl peroxide than with ultraviolet radiation,[266] but Haszeldine and co-workers have obtained excellent yields in additions to fluorinated olefins by irradiation

[259] Pietrusza, Sommer, and Whitmore, *J. Am. Chem. Soc.*, **70**, 484 (1948).
[260] El-Abbady and Anderson, *J. Am. Chem. Soc.*, **80**, 1737 (1958).
[261] Lipscomb, U.S. pat. 2,570,462 [*C.A.*, **46**, 6141 (1952)].
[262] Ernsberger and Lipscomb, U.S. pat. 2,570,463 [*C.A.*, **46**, 6141 (1952)].
[263] Speier and Webster, *J. Org. Chem.*, **21**, 1044 (1956).
[264] Freidlina, Chukovskaya, and Ts'ao, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **127**, 551 (1959).
[265] Fuchs and Gilman, *J. Org. Chem.*, **22**, 1009 (1957).
[266] McBee, Roberts, and Puerckhauer, *J. Am. Chem. Soc.*, **79**, 2329 (1957).

of the reactants in sealed quartz tubes[267-269] Among the other initiators azo compounds appear to be about as effective as benzoyl peroxide,[261,362] and γ-ray irradiation has been used to obtain high yields of adducts from a variety of olefins.[269] Ozone has been claimed to be an initiator in the addition of silanes to perhalogenated olefins[270] and iron pentacarbonyl[264] has been reported to promote addition of triethoxysilane, a compound with which peroxides and ultraviolet irradiation are quite ineffective[269]

The purely thermal reaction is satisfactory if the olefin does not polymerize readily and if the reactants and products have adequate stability at the required temperature (160–400°). These reactions are usually carried out in autoclaves under pressure, but it is possible to use a flow system with a hot tube (400–600°).[271,272] For the preparation of 1:1 adducts, the high-temperature reaction has two drawbacks. it favors telomerization with polymerizable olefins and β-halogen elimination with haloolefins (see discussion below).

The formation of higher telomers is frequently observed in silane additions to reactive olefins With ethylene or propylene, telomer formation is unimportant in the peroxide- or azo-catalyzed reactions[273] unless the reaction is performed under high pressure.[261] Good yields of telomers having up to about 6 olefin units are obtained, however, by thermal reaction at 250–350°[273] Trichlorosilane,[274,275] methyldichlorosilane,[275,276] phenyldichlorosilane,[273] and triethylsilane[273] have been telomerized with ethylene and with propylene under such conditions Telomer formation is also observed in the ultraviolet-catalyzed additions of trichlorosilane and dimethylsilane to tetrafluoroethylene.[267,277] With very readily polymerizable olefins such as acrylonitrile, methyl acrylate, and styrene, only telomers are obtained regardless of the initiator used[278] It is possible to control the extent of telomerization to a considerable degree by variation in reactant ratios Thus, in the reaction between trichlorosilane and tetrafluoroethylene,[277] an olefin-to-silane ratio of 1:4

[267] Geyer and Hazeldine, J. Chem Soc, 1957, 1038
[268] Geyer and Hazeldine, J Chem Soc, 1957, 3925
[269] Geyer, Hazeldine, Leedham, and Marklow, J Chem Soc, 1957, 4472
[270] Farbenfabriken Bayer, Brit pat. 764,288 [C.A., 51, 14786 (1957)]
[271] White and Rochow, J Am Chem Soc, 76, 3897 (1954)
[272] Midland Silicones, Ltd, Brit pat 752,700 [C A, 51, 7402 (1957)]
[273] Freidina, Bull Acad Sci. USSR, Div. Chem Sci (Engl Transl), 1957, 1353
[274] Nesmeyanov, Freidina, and Chukovskaya, Proc Acad Sci USSR, Chem Sect (Engl Transl), 113, 197 (1957)
[275] Freidina, Freidina, and Chukovskaya, Tetrahedron, 1, 248 (1957)
[276] Nesmeyanov, Freidina, and Chukovskaya, Proc Acad Sci. USSR, Chem Sect. (Engl. Transl), 112, 41 (1957)
[277] Haseldine and Marklow, J Chem Soc, 1956, 962
[278] Speier, Zimmerman, and Webster, J Am Chem Soc, 78, 2278 (1956)

gave the 1:1 adduct in 60% yield, while a ratio of 5:6 gave only 35% of this adduct along with 65% of higher telomers.

The direction of addition of silyl radicals to olefins can usually be predicted from consideration of the relative stabilities of the alternative intermediate radicals as discussed in the introduction to this chapter. Thus, with terminal olefins, the addition is normally to the terminal carbon atom. Two apparent exceptions were reported for the additions of trichlorosilane and methyldichlorosilane to 1,1,2-trichloro-3,3,3-trifluoropropene.[266] The products, **67** and **68**, probably arise through initial attack of the silyl radicals on the central carbon atom followed by $\beta$ elimination of a chlorine atom. The thermal addition of trichlorosilane

$$HSiCl_3 + CF_3C(Cl){=}CCl_2 \rightarrow CF_3C(SiCl_3){=}CCl_2$$
$$\underset{\textbf{67}}{}$$

$$HSi(CH_3)Cl_2 + CF_3C(Cl){=}CCl_2 \rightarrow CF_3C[Si(CH_3)Cl_2]{=}CCl_2$$
$$\underset{\textbf{68}}{}$$
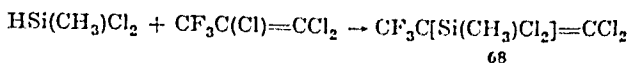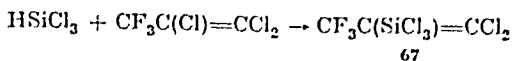
to chlorotrifluoroethylene is reported to yield both possible 1:1 adducts, **69** and **70**.[279,280] This is surprising in view of other radical additions to this olefin in which attack occurs exclusively on the $CF_2$ group. The photochemical reaction of trichlorosilane with chlorotrifluoroethylene yields only adduct **69**.[281]

$$Cl_3SiCF_2CHFCl \qquad\qquad Cl_3SiCFClCHF_2 \qquad\qquad (CH_3)_3SiC(SiCl_3){=}CHCH_3$$
$$\underset{\textbf{69}}{} \qquad\qquad\qquad \underset{\textbf{70}}{} \qquad\qquad\qquad\qquad \underset{\textbf{71}}{}$$
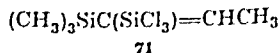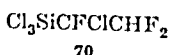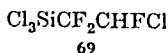
Additions to monosubstituted acetylenes occur at the terminal carbon atom.[282,283] The only disubstituted acetylene studied is trimethylsilylpropyne, which is reported to give the adduct **71** on peroxide-initiated addition of trichlorosilane.[284] In a recent study Benkeser and co-workers have shown that peroxide-initiated additions of trichlorosilane to 1-pentyne, 1-hexyne, 1-heptyne, and 3-methyl-1-butyne proceed stereoselectively to produce approximately 3:1 mixtures of *cis-* and *trans-*olefins.[283,285] The *trans*-olefin was the major product with 3,3-dimethyl-1-butyne.[285]

The additions of trichlorosilane to hexafluoro-1,3-butadiene at 200–250°[279,280] and to 1,3-butadiene at 330°[258] result in formation of the 1,2 rather than the 1,4 adducts.

A considerable number of compounds having one or more hydrogen

[279] Midland Silicones, Ltd., Brit. pat. 746,510 [*C.A.*, **51**, 7402 (1957)].
[280] Haluska, U.S. pat. 2,800,494 [*C.A.*, **51**, 17982 (1957)].
[281] Haszeldine and Young, *J. Chem. Soc.*, **1960**, 4503.
[282] Burkhard, *J. Am. Chem. Soc.*, **72**, 1402 (1950).
[283] Benkeser and Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).
[284] Shchukovskaya, Petrov, and Egoroft, *J. Gen. Chem. USSR (Engl. Transl.)*, **26**, 3713 (1956).
[285] Benkeser, Burrous, Nelson, and Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

atoms attached to silicon undergo free radical additions to olefins  Silane itself adds to ethylene at 450–510° in a flow system to give a mixture consisting largely of ethyl- and diethyl-silane together with disilanes, trisilanes, etc.[271]  With ultraviolet irradiation (mercury photosensitization), the major reaction products are ethylsilane, n-butylsilane, and ethanedisilane[271]  Stepwise additions of silane can be effected thermally to give products of the type RR'SiH, since higher temperature is required for reaction of the second hydrogen atom[286]  It has been concluded that, the higher the molecular weight of the olefin, the more readily it undergoes polysubstitution with silane  Thus isobutylene gives mainly tetra-isobutylsilane, even at 100°, while ethylene gives chiefly monoethylsilane up to about 200°.[286]

The presence of electronegative groups on silicon facilitates addition[259]  Trichlorosilane reacts much faster than methyldichlorosilane,[257,287] whereas trialkylsilanes and trialkoxysilanes react very slowly, if at all[257,259]  The reported reactivities of silanes seem to vary widely.  For example, whereas triethoxysilane is unreactive toward 1-octene with peroxides or ultraviolet radiation[259] and methyldi-n-propylsilane gives almost no adduct with 1-pentene under similar conditions,[257] methyl diethoxysilane is reported to give a 79% yield of adduct with n-heptafluoropropylethylene on ultraviolet irradiation for 3 days[259]  In additions to cyclooylefins, ultraviolet irradiation gives higher yields with tribromosilane than with trichlorosilane.[288,289]  Similarly, alkyl dibromosilanes appeared to be more reactive than alkyl dichlorosilanes with either ultraviolet or peroxide initiation.

Except for the presence of interfering functional groups such as hydroxyl or amino, there appear to be no limitations on the nature of the olefins to which silanes can be added.  Silanes have been added to ethylene, tetrafluoroethylene, tetramethylethylene, methyl oleate, cyclohexene, β-pinene, acrolein diethyl acetal, and a host of other olefins.  Not all silanes will add to every olefin, however.  Triphenylsilane, which gives good yields of adducts with straight-chain alkenes, does not add to cyclohexene.[290,291]  Allyl chloride reacts with trichlorosilane to give the 1:1 adduct in 20% yield,[259] but with phenylsilane complex products only are obtained.[278]  With readily polymerizable olefins, there is often a tendency to telomer formation, and this may be sufficient in certain

[283] Wolfs and Cook, U.S. pat  2,786,862 [C A , 51, 13304 (1957)]
[284] Seyferth and Rochow, J  Org Chem , 22, 250 (1955)
[285] Nametkin, Topchiev, and Charaykava, Proc Acad Sci USSR, Chem Sect (Engl Transl ), 111, 767 (1956)
[286] Topchiev, Nametkin, and Solovova, Doklady Akad Nauk SSSR, 86, 965 (1952) [C A , 47, 10471 (1953)]
[290] Gilman and Miles, J  Am Chem Soc , 60, 611 (1958)
[291] Merten and Gilman, J  Am Chem Soc , 76, 5798 (1954).

instances (e.g., styrene) to preclude the isolation of 1:1 adducts. Various statements can be found in the literature regarding the relationship of structure to reactivity. The following order of relative velocities of trichlorosilane addition (at 280°) to a series of substituted ethylenes suggests *no* strong steric influence: $CH_2{=}CH_2 < (CH_3)_2C{=}CH_2 < CH_3CH{=}CH_2 < C_2H_5CH{=}CH_2 < CH_3CH{=}CHCH_3 < (CH_3)_2C{=}CHCH_3 < (CH_3)_2C{=}C(CH_3)_2$.[292]

In additions to a series of olefins of the structure $X_3SiCH_2CH{=}CH_2$, electronegative groups on silicon (X = $C_6H_5$ or Cl) are reported to activate the double bond.[293] Also, when X is an alkyl group, the activity of the double bond increases with increasing size of the substituent.

A surprising lack of reactivity has been noted with perfluoropropylene, which readily undergoes free radical additions of thiols, hydrogen bromide, etc., but gives only traces of adduct with trichlorosilane in the presence of peroxides or ultraviolet radiation.[266] Prolonged heating at 180° gave no adduct,[290] while at 200–300° a 14% yield of adduct was obtained.[279] Other fluorinated olefins, including tetrafluoroethylene, 3,3,3-trifluoropropene, and 2,3,3,4,4,4-hexafluoro-1-butene are quite reactive and give adducts in high yield.[266,269] No reaction occurs between phenylsilane and allyl cyanide or allylmercaptotrimethylsilane when *t*-butyl perbenzoate is used as catalyst.[278] Under the same conditions, allyl alcohol and allylamine give only complex products, presumably because of interaction of the Si—H hydrogen atoms with the hydroxyl or amino groups. Protection of the hydroxyl group of allyl alcohol by a trimethylsilyl group permits the reaction to proceed normally.

Reaction of silanes with chloroethylenes frequently results in the formation of vinylsilanes rather than saturated 1:1 adducts.[294–296] This is especially true at higher temperatures, although mixtures of the saturated adduct and the vinylsilane sometimes result from peroxide- or ultraviolet-initiated reactions at moderate temperatures.[297] At 500–600°, the sole product of reaction between trichlorosilane and tetrachloroethylene is trichlorovinyltrichlorosilane (72), while at 125° with peroxide initiators the product is a mixture of 72 (12.6 parts) and 1,1,2,2-tetrachloroethyl trichlorosilane (73) (4.7 parts).[297]

$$Cl_3SiCCl{=}CCl_2 \qquad\qquad Cl_3SiCCl_2CHCl_2$$
$$\textbf{72} \qquad\qquad\qquad\qquad \textbf{73}$$
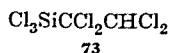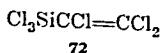
[292] Voronkov, Romanova, and Smirnova, *Chem. Listy*, 52, 640 (1958) [*C.A.*, 52, 13615 (1958)].

[293] Topchiev, Nametkin, Chernyskeva, and Durgar'you, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 110, 545 (1956).

[294] Midland Silicones, Ltd., Brit. pat. 737,963 [*C.A.*, 50, 10760 (1956)].

[295] Agre and Hilling, *J. Am. Chem. Soc.*, 74, 3895 (1952).

[296] Mironov and Leites, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1959, 1957.

[297] McBee, Roberts, and Puerckhauer, *J. Am. Chem. Soc.*, 79, 2326 (1957).

The formation of these unsaturated products occurs not as a result of dehydrohalogenation of the 1.1 adduct, but through $\beta$-elimination of a halogen atom from the intermediate radical.[295] A method for preparing

$$R_3SiCCl_2CCl \rightarrow R_3SiCCl=CCl_2 + Cl$$
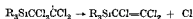
vinylsilanes consists in passing a mixture of the appropriate silane and vinyl chloride through a quartz tube at 550–600° [272] In this way, vinyltrichlorosilane was obtained in 53% yield from trichlorosilane and methylvinyldichlorosilane in 59% yield from methyldichlorosilane.

Another example of what is apparently a $\beta$-elimination occurs in the thermal reaction between trichlorosilane and 2,4,4-trimethyl-1-pentene.[292,298]

$$HSiCl_3 + CH_2=C(CH_3)CH_2C(CH_3)_3 \xrightarrow{Heat} Cl_3SiCH_2C(CH_3)=CH_2 + (CH_3)_3CH$$
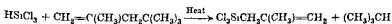
The addition of trichlorosilane to $\beta$-pinene[299–302] proceeds with carbon skeleton rearrangement in a manner entirely analogous to that observed in the addition of chloroform.[303] The resultant 1.1 adduct has the structure 74.[302] In the presence of a large excess of trichlorosilane, a second molecule of the silane adds to give the adduct 75



under prolonged ultraviolet irradiation, a second molecule of the silane adds to give the adduct 75

## Comparison with Other Methods

A number of different methods are available for the formation of silicon-carbon bonds. The most important are (1) the reaction of Grignard reagents or other organometallics with halosilanes or alkoxysilanes, (2) the direct synthesis from silicon and alkyl or aryl halides, (3) the Wurtz-Fitting condensation of silicon halides with organic halides, and (4) the metal and metal salt-catalyzed additions of silanes to alkenes

[298] Plueddemann, U.S. pat. 2,647,447 [C.A., 48, 5206 (1954)]
[299] Goldblatt and Okroyd, U.S. pat. 2,533,240 [C.A., 45, 2262 (1931)].
[300] Fraunel, Bull Soc Chim. France, 1953, 792
[301] Fraunel and Calas, Compt Rend, 240, 203 (1955).
[302] Calas and Fraunel, Compt Rend, 243, 595 (1956).
[303] du Pont, Dulou, and Clement, Bull. Soc. Chim. France, 1951, 257.

and alkynes. These and other methods are treated at some length by other authors.[304]

From the standpoint of its relationship to the work discussed above, the metal- and metal salt-catalyzed addition of silanes to unsaturates warrants some additional comment. The most commonly used metal and metal salt catalysts are platinum on charcoal or on $\gamma$-alumina, chloroplatinic acid, potassium chloroplatinate, or palladium. Ruthenium chloride, osmium tetroxide on carbon, and several other compounds of these elements have also been used. This method overlaps the free radical-catalyzed reaction to a considerable extent, and it frequently affords improved yields of product. This is especially true for additions to acetylenes.[283,284] 1-Hexyne gives a 36% yield of adduct with trichlorosilane in the peroxide-initiated reaction, but a 93% yield with a platinum-on-charcoal catalyst. Phenylacetylene fails to give any adduct with peroxide but gives an 82% yield with the platinum-on-carbon catalyst.[283] These catalysts permit the preparation of simple adducts from readily polymerizable olefins such as styrene or acrylonitrile, a feat either difficult or impossible under free radical conditions.[305] Despite the considerable overlap between these two methods, there exist certain differences of important synthetic consequence:

(*i*) Whereas the free radical-catalyzed additions are almost never accompanied by rearrangement, this is not true for the ionic (metal- or salt-catalyzed) additions. The ionic additions of trichlorosilane and of methyldichlorosilane to 3-heptene and 2-pentene give the *n*-heptyl and *n*-pentyl adducts exclusively.[305,306]

(*ii*) Additions of silanes to acetylenes proceed stereoselectively to give the *trans*-olefin with free radical catalysts and the *cis*-olefin with ionic catalysts.[283,285]

(*iii*) With butadiene, metal-catalyzed addition yields the 1,4 adduct,[307] while the thermal (free radical) reaction gives the 1,2 adduct.[258]

The use of platinum catalysts with perhalogenated olefins is reported to result in explosions on occasion.[308] Hence due caution should be observed with such systems.

A variety of other catalysts have been used with varying degrees of success for the addition of silanes to unsaturates. Among these should be mentioned amines such as triethylamine, pyridine, and piperidine.[309]

[304] Eaborn, *Organosilicon Compounds*, Academic Press, Inc., New York, 1960.
[305] Speier, Webster, and Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).
[306] Saam and Speier, *J. Am. Chem. Soc.*, **80**, 4104 (1958).
[307] Wagner, U.S. pat. 2,637,738 [*C.A.*, **48**, 8254 (1954)].
[308] Tarrant, Dycken, Dunmire, and Butler, *J. Am. Chem. Soc.*, **79**, 6536 (1957).
[309] Nozakura, *Bull. Chem. Soc. Japan*, **29**, 322, 326, 784 (1956).

## Experimental Conditions

The experimental conditions for effecting the free radical addition of silanes to olefins are usually simple and straightforward  The silane and olefin are mixed, the initiator (peroxide or azo) added, and the mixture heated or, alternatively, the mixture is irradiated with ultraviolet or ionizing radiation.  Solvents are rarely used, excess of the silane generally serving this function  With olefins that are susceptible to telomerization a large excess of the silane is necessary to obtain good yields of the 1.1 adducts  It is sometimes advantageous to add a mixture of the olefin and initiator to the heated silane, especially if the silane contains more than one hydrogen atom and the monoadduct is desired.[278]  A favorable attribute of this system, as of free radical-initiated additions in general, is the simplicity of isolation of the product  Fractional distillation is usually all that is required.

## ADDITION OF GERMANES TO OLEFINS

Additions of germanes to olefins are analogous to the additions of silanes.  However, the germane reaction has been studied less extensively.  The examples reported include additions of trichlorogermane, trialkylgermanes, and triphenylgermane to various olefins.  The reaction is apparently free radical in nature, since telomers are sometimes formed,[310] and initiation by peroxides or ultraviolet light is frequently required.[310-312]  Evidence has recently been presented that organotin hydrides, which in contrast to silanes and germanes have been considered to undergo solely ionic addition to olefins,[313,314] do add by a free radical process.[3c]

Germanes are more reactive than the corresponding silanes in free radical additions.  Thus, in the absence of initiators, temperatures in the range 160–400° are required to effect the addition of silanes to olefins,[258] while trichlorogermane adds exothermally to various olefins at room temperature,[315] and trialkylgermanes add to acrylonitrile and acrylate esters at the reflux temperature.  The difference in reactivity is illustrated further by the observation that triphenylgermane adds to triphenylallylgermane in 85% yield under peroxide initiation, whereas triphenylsilane fails to add under similar conditions [311]

[310] Leabre and Satgé, Compt  Rend , 247, 471 (1958).
[311] Gilman and Gerow, J. Am  Chem. Soc., 79, 342 (1959).
[312] Steen and Gilman, J. Org. Chem , 22, 684 (1957).
[313] Van der Kerk, Luijten, and Noltes, Chem  & Ind (London), 1956, 352
[314] Fuchs and Gilman, J. Org. Chem , 22, 1009 (1957).
[315] Petrov, Mironov, and Dzhurinskaya, Proc. Acad. Sci. USSR, Chem Sect (Engl Transl.)
128, 739 (1959)

Triphenylgermane fails to add to 1,1-diphenylethylene with peroxide or ultraviolet initiation, and in its reaction with cyclohexene some tetraphenylgermane[314] is formed in addition to the 1:1 adduct.

The experimental conditions for reaction of germanes with olefins can be inferred from those of the silanes, bearing in mind the generally greater reactivity of the germanes.

# RADICAL ADDITIONS
## TO FORM PHOSPHORUS-CARBON BONDS*

### Compounds Containing P—H Bonds

The free radical addition to olefins of a variety of phosphorus compounds containing P—H bonds is a general reaction. Examples involving phosphine,[316-318] substituted phosphines,[318,319] phosphorous acid

$$\underset{/}{\overset{\backslash}{\text{P}}}-\text{H} + \underset{|}{\overset{|}{\text{C}}}=\underset{|}{\overset{|}{\text{C}}} \rightarrow \underset{/}{\overset{\backslash}{\text{P}}}-\underset{|}{\overset{|}{\text{C}}}-\underset{|}{\overset{|}{\text{C}}}\text{H}$$
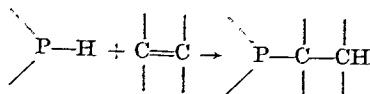
[HP(O)(OH)$_2$][220,321] and esters,[222-225] hypophosphorous acid [H$_2$P(O)OH][325] and salts,[327,328] and phosphinic acid derivatives [RPH(O)OR][327] have been reported. Although no extensive studies of mechanism have been made, it seems certain that the reactions occur by a radical chain mechanism, written here for addition of a dialkyl phosphite.[317,324]

In this scheme, the (RO)$_2$OP· radical is the adding species, and, in the

$$(\text{RO})_2\text{OPH} \xrightarrow{\text{Initiator}} (\text{RO})_2\text{OP·}$$

$$(\text{RO})_2\text{OP·} + \underset{|}{\overset{|}{\text{C}}}=\underset{|}{\overset{|}{\text{C}}} \longrightarrow (\text{RO})_2\text{OP}\underset{|}{\overset{|}{\text{C}}}-\underset{|}{\overset{|}{\text{C}}}·$$
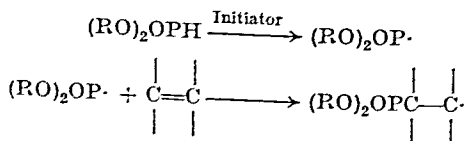
* Phosphorus addition reactions, ionic and radical, have been reviewed by Crofts.[329] Radical additions have been discussed by Walling (ref. 45, p. 341).

[316] N. V. deBataaf. Pet. Maats., Brit. pat. 673,451 [C.A., 47, 5426 (1953)].

[317] Stiles, Rust, and Vaughan, J. Am. Chem. Soc., 74, 3282 (1952).

[318] Rauhut, Currier, Semsel, and Wystrach, J. Org. Chem., 26, 5138 (1961).

[319] Arbuzov, Vinokurova and Perfil'eva, Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.), 127, 657 (1959).

[320] Griffin, J. Org. Chem., 25, 665 (1960).

[321] Griffin and Wells, J. Org. Chem., 24, 2049 (1959).

[322] Barnes and David, J. Org. Chem., 25, 1191 (1960).

[323] Kharasch, Mosher, and Bengelsdorf, J. Org. Chem., 25, 1000 (1960).

[324] Stiles, Vaughan, and Rust, J. Am. Chem. Soc., 80, 714 (1958).

[325] Bittles and Joyce, U.S. pat. 2,559,754 [C.A., 46, 1026 (1952)].

[326] Williams and Hamilton, J. Am. Chem. Soc., 77, 3411 (1955).

[327] Stiles and Rust, U.S. pat. 2,724,718 [C.A., 50, 10124 (1956)].

[328] N. V. deBataaf. Pet. Maats., Brit. pat. 660,918 [C.A., 46, 8145 (1952)].

[329] Crofts, Quart. Rev. (London), 12, 341 (1958).

$$(RO)_2OPC\text{—}C + (RO)_2PH \longrightarrow (RO)_2OPC\text{—}CH + (RO)_2OP$$

$$(RO)_2OPC\text{—}C + C=C \longrightarrow (RO)_2OPC\text{—}C\text{—}C\text{—}C$$

$$(RO)_2OPC\text{—}C\text{—}C + (RO)_2PH \longrightarrow$$

$$(RO)_2OPC\text{—}C\text{—}C\text{—}CH + (RO)_2OP \quad \text{etc}$$
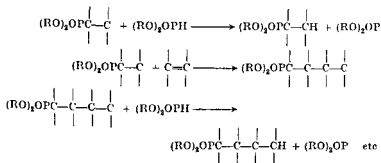
products whose structures have been determined, the phosphorus atom is found on the carbon atom ordinarily attacked by radicals   Reversibility in the addition step has been demonstrated in the additions of phenylphosphine, 2-cyanoethylphosphine, and di-n-butylphosphine to cis-2-butene [330]   Other aspects of the mechanism and stereochemistry have not been investigated.

Reactions of phosphine and substituted phosphines with olefins have been initiated by ultraviolet radiation, x-radiation, peroxides, and azo catalysts   Additions of phosphine have been carried out with terminal, internal, and cyclic olefins. With terminal olefins, all the P—H bonds can participate. Thus from 1-octene, octyl (0–55%), dioctyl (0–93%), and trioctyl (4–100%) phosphine are formed, the relative yields depending on the ratio of starting materials.[318]

$$PH_3 + CH_2=CHC_6H_{13} \cdot n \xrightarrow{\text{Ascuite-}n} n\text{-}C_8H_{17}PH_2 + (n\text{-}C_8H_{17})_2PH + (n\text{-}C_8H_{17})_3P$$

With isobutylene and cyclohexene, steric problems arise in the addition of the third molecule of olefin, so that triisobutylphosphine is formed in low yield and tricyclohexylphosphine not at all, even though good yields of the mono- and di-adducts are formed   With easily polymerizable olefins, e.g., styrene and ethyl acrylate, conversions in good yield to the mono-, di-, and tri-adducts are accompanied by relatively small amounts of telomerization   This indicates that chain transfer on the P—H bonds of phosphines occurs readily.   The major product from the ultraviolet-initiated reaction with allyl chloride is a hard insoluble phosphorus-containing polymer.[327]   Phosphine has been added to several fluoroolefins at 150° without added catalysts [331]   From tetrafluoroethylene a mono- and a di-adduct are obtained in addition to tetrafluoroethylene

$$PH_3 + CF_2=CF_2 \longrightarrow CHF_2CF_2PH_2 + (CHF_2CF_2)_2PH + H_2PCF_2CF_2PH_2$$
diphosphine.   It is not clear whether or not these are free radical reactions.
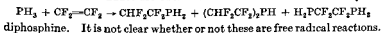
[330] Pellon, J. Am Chem Soc, 83, 1915 (1961).

[331] Parshall, England, and Lindsey, J Am Chem Soc, 81, 4801 (1959)

Mono- and di-substituted phosphines have been used to prepare unsymmetrical secondary and tertiary phosphines;[318] for example, 2-cyanoethylphosphine and 1-octene form monoöctyl- and dioctyl-2-cyanoethylphosphine.

$$CNCH_2CH_2PH_2 + CH_2{=}CHC_6H_{13}\text{-}n \rightarrow$$

$$CNCH_2CH_2PHC_8H_{17}\text{-}n + CNCH_2CH_2P(C_8H_{17}\text{-}n)_2$$
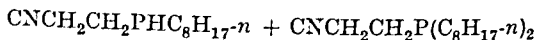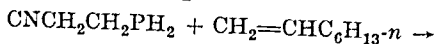
Dibutylphosphine reacts with butadiene via 1,4 addition to form dibutyl-2-*trans*-butenylphosphine and a small amount of a 2:1 adduct whose structure has not been determined.

$$(C_4H_9)_2PH + CH_2{=}CHCH{=}CH_2 \rightarrow (C_4H_9)_2PCH_2CH{=}CHCH_3 + 2{:}1 \text{ adduct}$$
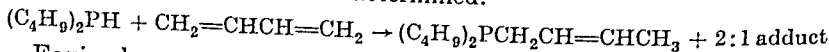
Equimolar amounts of 2-cyanoethylphosphine and 1-heptyne form 2-cyanoethyl-bis-(1-heptenyl)phosphine in a 26% yield accompanied by only a trace of the intermediate monoadduct.[318] Bis-(2-cyanoethyl)-

$$CNCH_2CH_2PH_2 + HC{\equiv}CC_5H_{11}\text{-}n \rightarrow$$

$$CNCH_2CH_2P(CH{=}CHC_5H_{11}\text{-}n)_2 + CNCH_2CH_2PHCH{=}CHC_5H_{11}\text{-}n$$
$$\text{(trace)}$$
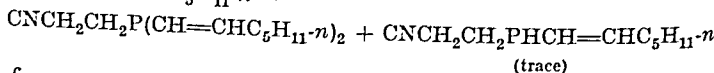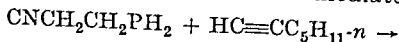
phosphine forms a monoadduct with 1-heptyne. In neither of these cases are products found which result from further addition of phosphine to the unsaturated adducts.

The ultraviolet- or peroxide-initiated additions of phosphorous acid have given yields of 18–28% of 1:1 adducts (phosphonic acids), the major products being higher telomers or polymers of the olefin.[320,321] In several cases, e.g., 1-octene, 1-hexene, and 1-decene, the 2:1 adducts have been isolated and have been shown to be those resulting from a conventional head-to-tail telomerization.[320]

$$HP(O)(OH)_2 + CH_2{=}CHC_4H_9\text{-}n \xrightarrow{\text{Peroxide}}$$

$$n\text{-}C_6H_{13}P(O)(OH)_2 + \begin{array}{c} n\text{-}C_4H_9 \\ \diagdown \\ CHCH_2P(O)(OH)_2 \\ \diagup \\ n\text{-}C_6H_{13} \end{array}$$
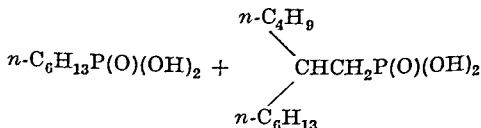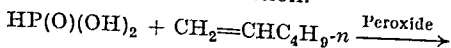
The peroxide-initiated additions of aqueous hypophosphorous acid to terminal olefins have been used to prepare dialkylphosphinic acids in yields up to 40%.[326] No 1:1 adducts were reported. Analogous additions of sodium hypophosphite have been reported to give high yields of 1:1 adducts.[327,328,332]

$$H_2P(O)OH + CH_2{=}CHR \rightarrow (RCH_2CH_2)_2P(O)OH$$
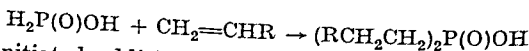
Peroxide-initiated additions of a phosphinic ester, $C_6H_5PH(O)OC_2H_5$, and the sodium salt of a phosphinic acid, $n\text{-}C_6H_{13}PH(O)ONa$, to terminal olefins gave the expected 1:1 adducts.[327,328]

[332] Smith, U.S. pat. 2,648,695 [*C.A.*, 48, 8252 (1954)].

Of all the additions of compounds containing P—H bonds, those involving dialkyl phosphites to give dialkylphosphonates have received the most attention. They have been initiated with peroxides, azonitriles, and ultraviolet radiation. The ratio of reactants affects both the rate of

$$HP(O)(OR)_2 + CH_2=CHR \rightarrow RCH_2CH_2P(O)(OR)_2$$

the reaction and the composition of the product [324] A high concentration of the dialkyl phosphite results in a long kinetic chain and a predominance of the 1.1 adduct, while a high concentration of the olefin shortens the chain length and results in greater proportions of higher telomers [333] The effect of high olefin concentration on the rate indicates that the olefin is actually an inhibitor of the addition reaction The mechanism for this inhibition no doubt involves abstraction of allylic hydrogen by the intermediate radical resulting in the formation of a stable allylic radical, thus effectively interrupting the kinetic chain Both effects of high olefin concentration, i e, telomerization and hydrogen abstraction, are attributable to relatively low chain transfer constants for dialkyl phosphites [324] Similar arguments have been applied to correlate the results in phosphorous acid additions [320,321]

Both terminal and internal olefins readily undergo radical addition of dialkyl phosphites Ethylene and tetrafluoroethylene yield telomers with dialkyl phosphites, the length of the carbon chain depending on the olefin pressure employed [325,335,336] Additions to terminal olefins form 1:1 adducts with the phosphorus atom attached to the terminal carbon. The additions of diethyl phosphite to 2 hexene and 2-heptene are reported to proceed at a lower rate than the corresponding additions to terminal olefins, and to yield a single 1·1 adduct with phosphorus in the 2 position in each case [337]

In one example of the addition of a dialkyl phosphite to an α,β-unsaturated ester reported, both 1:1 adducts were found [327,328] This result is surprising, since in other radical additions to α,β-unsaturated



$$(n\text{-}C_4H_9O)_2(O)PH + CH_2CH=CHCO_2C_2H_5 \xrightarrow{\text{Peroxide}} \begin{cases} (n\text{-}C_4H_9O)_2P(O)CHCH_3CO_2C_2H_5 \quad (CH_3) \\ (n\text{-}C_4H_9O)_2P(O)CHCO_2C_2H_5 \quad (C_2H_5) \end{cases}$$
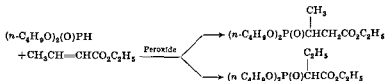
[332] Pless, Myers, and Jensen, J. Am. Chem. Soc., 77, 6225 (1955).
[334] Sasin, Olszewski, Russell, and Swern, J. Am. Chem. Soc., 81, 6275 (1959)
[335] Rauford and Joyce, U.S. pat. 2,478,390 (C.A. 44, 1126 (1950)]
[336] Bruce, J. Org. Chem, 26, 3197 (1961)
[337] Pudovik and Konovalova, J. Gen. Chem. USSR (Engl. Transl), 29, 3305 (1959).

esters (e.g., the addition of phosphine to methyl acrylate) only $\beta$-substituted esters have been reported. Base-catalyzed additions of compounds containing P—H bonds to $\alpha,\beta$-unsaturated carbonyl compounds and nitriles have been studied extensively,[329] but apparently no comparative study of the two methods has been made. Both a base-catalyzed and a free radical addition of diethyl phosphite to vinyl acetate have been realized.[338]

$$CH_3CO_2CH{=}CH_2$$
$$+HP(O)(OC_2H_5)_2 \underset{\text{Peroxide}}{\overset{\text{NaOC}_2\text{H}_5}{\longrightarrow}} \begin{cases} CH_3CO_2CH(CH_3)P(O)(OC_2H_5)_2 \\ \\ CH_3CO_2CH_2CH_2P(O)(OC_2H_5)_2 \end{cases}$$
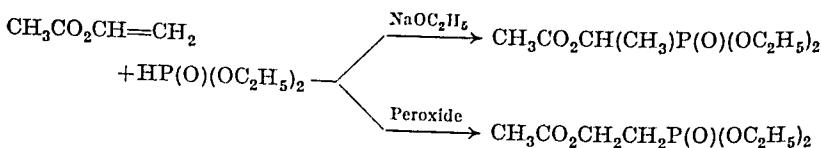
Attempts to add dialkyl phosphites to unactivated double bonds thermally or with acid and base catalysts have been unsuccessful.[337] Similarly, the addition of phosphorous acid to terminal olefins did not occur thermally or under acid catalysis.[321] It thus appears that, in contrast to additions of thiols, it is not possible to add compounds containing P—H bonds to unactivated olefins except by a radical procedure.

There have been no studies of additions of dialkyl phosphites to acetylenes.

A few ultraviolet- and peroxide-initiated additions of esters of thiophosphorous acid have been reported.[339] These esters are apparently more reactive in additions than their oxygen counterparts.

$$HP(S)(OR)_2 + CH_2{=}CHC_6H_{13}\text{-}n \rightarrow n\text{-}C_8H_{17}P(S)(OR)_2$$
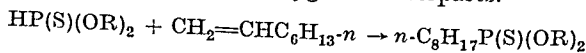
## Other Phosphorus Compounds

A peroxide-initiated addition of phosphorus trichloride to olefins giving 1:1 adducts and higher-boiling materials of undetermined nature was reported in 1945 by Kharasch, Jensen, and Urry.[340] A typical free radical chain mechanism in which the dichlorophosphine radical is the adding

$$RCH{=}CH_2 + PCl_3 \xrightarrow{\text{Peroxide}} RCHClCH_2PCl_2$$

species was proposed.

$$PCl_3 \rightarrow PCl_2{\cdot} + Cl{\cdot}$$
$$PCl_2{\cdot} + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2PCl_2$$
$$R\dot{C}HCH_2PCl_2 + PCl_3 \rightarrow RCHClCH_2PCl_2 + PCl_2{\cdot}$$
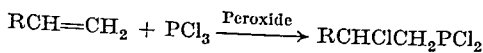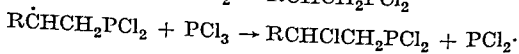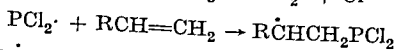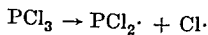
There has apparently been no further study of this reaction.

[338] McConnell and Coover, *J. Am. Chem. Soc.*, **79**, 1961 (1957).
[339] Pudovik and Konovalova, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 2328 (1960).
[340] Kharasch, Jensen, and Urry, *J. Am. Chem. Soc.*, **67**, 1864 (1945).

Somewhat related to the foregoing reaction is the oxidative phosphonation of olefins by oxygen and phosphorus trichloride.[341,342] From 2-butene, 2-chlorobutyl-3 phosphonic dichloride was obtained, presumably by the radical addition of the elements of Cl and $POCl_2$. With 1-butene both 1.1 adducts were formed in addition to 2-chlorobutyl-3-

$$CH_3CH=CHCH_3 + PCl_3 + O_2 \rightarrow CH_3CHClCH(CH_3)POCl_2$$
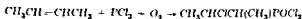
phosphonic dichloride  The last product could arise from a radical

$$CH_3CH_2CH=CH_2 + PCl_3 + O_2 \rightarrow CH_3CH_2CHClCH_2POCl_2$$
$$+ CH_3CH_2CH(CH_2)POCl_2 + CH_3CH_2P(OCl_2)CHClCH_3$$
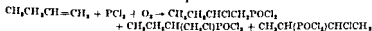
substitution by the $POCl_2$ radical at the allylic position followed by ionic addition of hydrogen chloride.  Further work is needed to define the mechanism of this reaction.  An attempt to achieve the addition of diethyl phosphorochloridate, $(C_2H_5O)_2P(O)Cl$, to 1-octene by a free radical procedure was unsuccessful.[323]  The additions of phosphorus pentachloride to olefins are presumably ionic reactions.

Free radical-induced reactions of alkyl and aryl dihalophosphines with olefins and dienes result largely in the formation of copolymers, in some cases (especially with dienes) approaching a 1:1 composition.[343–346]  Isoprene and phenyldichlorophosphine furnish a 1:1 copolymer in 45% yield.  This reaction does not involve scission of P—Cl bonds followed by

$$C_6H_5PCl_2 + CH_2=CHC=CH_2 \xrightarrow[Azonitrile]{CH_3} \left[\begin{array}{c} CH_3 \\ -CH_2CH=C-CH_2-P- \\ | \quad\quad | \\ Cl \quad Cl \end{array}\right]_n \begin{array}{c} C_6H_5 \\ | \\ \end{array}$$
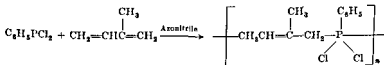
addition to the olefin, but rather is apparently analogous to the radical copolymerization of sulfur dioxide with olefins.

White phosphorus reacts with oxygen and olefins in benzene solution by a radical chain process to form products with the approximate composition (olefin $P_4O_4$).[347]  On the basis of hydrolysis studies these materials have been assigned a polymeric anhydride structure in which one phosphorus atom is bound to carbon in a phosphonic anhydride function and the other is linked to carbon through oxygen and is in the phosphite oxidation

[341] Zinov'ev and Soborovskii, *J Gen Chem, USSR*, (*Engl, Transl* ), 29, 611 (1959)

[342] Soborovskii, Zinov'ev, and Mukr, *Doklady Akad Nauk SSSR*, 109, 98 (1956) [*C A , 51*, 1825 (1957)]

[343] McCormack, U S pat 2,671,677 [*C.A.*, 48, 6737 (1954)]

[344] McCormack, U S pat 2,671,079 [*C A*, 48, 6738 (1954)]

[345] McCormack, U S pat 2,671,078 [*C A*, 48, 6738 (1954)]

[346] McCormack, *Reactions of Dienes with Phosphorus Compounds.* Gordon Research Conferences, 1957.

[347] Walling, Stacey, Jamison, and Huyser, *J. Am. Chem Soc* , 80, 4543, 4546 (1958)

level; for example, structure **76** has been proposed for the product from cyclohexene. The reaction is apparently general and the yields high



76
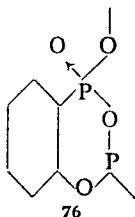
(70–100%). With 1-octene and olefins of higher molecular weight, further oxidation leads to products approaching the composition (olefin ·$P_2O_5$).

## Experimental Conditions

The usual free radical initiators, e.g., peroxides, azonitriles, and ultraviolet radiation, are effective. In order to attain maximum yields of 1:1 adducts, a 1.5-fold or larger excess of the phosphorus compound is desirable. The peroxide-initiated reactions of dialkyl phosphites[338] and phosphonates[322] have generally been carried out without solvents in sealed Pyrex tubes or metal autoclaves at the decomposition temperatures of the initiators. Open vessels can be used with high-boiling reactants.[324] In ultraviolet experiments, temperatures ranging from room temperature to 100° have been used.[337] In ultraviolet-initiated reactions with phosphine, the reactants are manipulated in a vacuum train, sealed in tubes, and irradiated at approximately room temperature.[317] Peroxide- and azonitrile-initiated additions of phosphine have been done in heptane solution in stainless steel autoclaves.[318] The peroxide-initiated additions of phosphorous[321] and hypophosphorous acids[326] have been carried out in aqueous solution.

## RADICAL ADDITIONS TO FORM CARBON-NITROGEN BONDS

The most important additions to olefins of radicals bearing the odd electron on nitrogen are the additions of dinitrogen tetroxide and nitryl chloride. Possibly the reactions of dinitrogen trioxide with olefins are homolytic,[348] but the present evidence suggests that dinitrogen pentoxide reacts ionically,[349] as does nitrosyl chloride generally. A recent paper indicates, however, that the addition of nitrosyl chloride to fluorinated

[348] Shechter and Ley, *Chem. & Ind. (London)*, 1955, 535.
[349] Stevens and Emmons, *J. Am. Chem. Soc.*, 79, 6008 (1957).

olefins is a free radical process [339]  Very few additions of amino radicals to olefinic double bonds have been reported [351]

The reaction of dinitrogen tetroxide with olefins and acetylenes has been studied for many years, but it was not until the studies of Levy, Scaife, and co-workers[352–354] in the 1940's that control of the reaction to give isolable products in good yield was accomplished. The earlier work generally resulted in the formation of unstable solids or oils from which the isolation of pure compounds was difficult or impossible  The reports of this early work are often conflicting, confused by questions of the nature and purity of the nitrogen oxides used and by lack of consistent nomenclature  Also, because of the unstable nature of many of the products, the analyses are frequently open to question and hence many of the interpretations and conclusions must be considered questionable  Riebsomer[355] has reviewed the reactions of dinitrogen tetroxide up to 1945  In view of the existence of this review and the points noted regarding the older literature on this subject, the discussion and tabulation which follow deal only with work appearing since 1945

By contrast, practically all the studies of the additions of nitryl chloride are recent, and the customary attempt at complete coverage has been made. Discussion of the related dinitrogen tetroxide-halogen systems is included with that of nitryl chloride.

## Dinitrogen Tetroxide

**Mechanism.** The studies of Levy and co-workers[352–354] showed that under properly controlled conditions the only products resulting from reaction of dinitrogen tetroxide with olefins are the *vicinal* dinitroalkane and nitro-nitrite, and that with unsymmetrical olefins the nitro group is always found on the carbon atom bearing the greater number of hydrogen atoms  In practice the products isolated are the dinitroalkane, the nitroalcohol, and some nitro-nitrate. The latter two products arise from hydrolysis and oxidation, respectively, of the nitronitrite.  These observations are rationalized by the assumption of a

$$RCH=CH_2 + N_2O_4 \rightarrow RCH(NO_2)CH_2NO_2 + RCH(ONO)CH_2NO_2$$
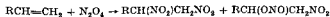
heterolytic cleavage of the tetroxide to $NO_2^+NO_2^-$ and subsequent addition  More recent studies of the reaction, however, support a free radical

[339] Park, Stefani, and Lacher, *J Org Chem*, **26**, 4017 (1961).

[351] Allinetti et al , *J Am Chem Soc*, **81**, 1489 (1959)

[352] Levy and Scaife, *J Chem Soc*, **1946**, 1093, 1096, 1100

[353] Levy, Scaife, and Wilder Smith, *J Chem Soc*, **1946**, 52

[354] Levy and Rose, *Quart Rev (London)*, **1**, 358 (1948)

[355] Riebsomer, *Chem Rev*, **36**, 157 (1945).

mechanism initiated by a homolytic dissociation of the dinitrogen tetroxide.

$$N_2O_4 \rightarrow 2NO_2\cdot$$

$$\cdot NO_2 + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2NO_2$$

Chain process:

$$R\dot{C}HCH_2NO_2 + N_2O_4 \rightarrow RCH(NO_2)CH_2NO_2 \quad or$$

$$RCH(ONO)CH_2NO_2 + \cdot NO_2$$

Non-chain process:

$$R\dot{C}HCH_2NO_2 + (O\dot{N}O \leftrightarrow \cdot ONO) \rightarrow RCH(NO_2)CH_2NO_2 \quad or$$

$$RCH(ONO)CH_2NO_2$$
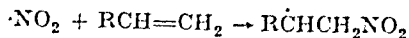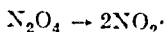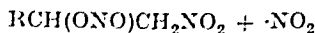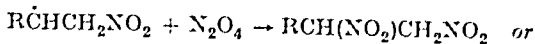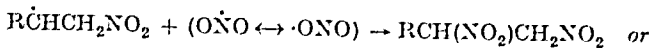
There is at present no evidence permitting a decision between the chain and non-chain processes. The principal evidence for the free radical nature of the addition can be summarized as follows: (1) The orientation in addition to unsymmetrical olefins is always specific and is not altered by the electronic character of substituents on the unsaturate.[356] (2) In the addition of dinitrogen tetroxide to methyl acrylate, there is formed, along with the expected dinitro adduct and nitro-nitrite, an appreciable amount of nitrogen-containing polymer. (3) In the presence of such well-known chain transfer agents as bromotrichloromethane,[357,358] bromoform,[359] or iodine,[360] formation of the normal adducts is suppressed, and the products obtained are those expected from interaction of a $\beta$-nitroalkyl radical with the transfer agent.

The addition of dinitrogen tetroxide exhibits stereoselectivity with a number of olefins. Cyclohexene and cyclopentene give both *cis-* and *trans-*nitro-nitrite adducts, the *trans* isomers predominating (58% and 84%, respectively). 1-Methylcyclohexene yields *trans-*1-methyl-2-nitrocyclohexyl nitrite exclusively.[358] Similarly 9,10-octalin gives only *trans-*9,10-dinitrodecalin, and the major attack on norbornylene occurs in an *exo-cis* direction.[361] (See equation on p. 227.)

The most thoroughly investigated olefin from a stereochemical viewpoint is stilbene. *cis-*Stilbene is converted to *trans-*stilbene under the reaction conditions used. Addition to *trans-*stilbene gives mixtures of *meso-* and *dl-*dinitrodiphenylethane in a 2:3 ratio, and of *erythro-* and

[356] Shechter and Conrad, *J. Am. Chem. Soc.*, **75**, 5610 (1953).

[357] Brand and Stevens, *Chem. & Ind.* (*London*), 1956, 469.

[358] Brand and Stevens, *J. Chem. Soc.*, 1958, 629.

[359] Baryshnikova and Titov, *Doklady Akad. Nauk SSSR*, **91**, 1099 (1953) [*C.A.*, **48**, 10629 (1954)].

[360] Stevens and Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

[361] J. J. Gardikes, Doctoral Dissertation, Ohio State University, 1960; *Dissertation Abstrs.*, **21**, 757 (1960).

*threo*-1-hydroxy-2-nitro-1,2-diphenylethane (from the nitro-nitrite after hydrolysis) in about a 1:2 ratio, when the reaction is carried out in ether
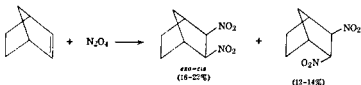


in the absence of oxygen.[362,363] Thus the major isomers are those deriving from *cis* rather than *trans* addition, and it has been suggested that these major isomers are formed more rapidly because the structure of the transition state for reaction of the 2-nitro-1,2-diphenyl-1-ethyl radical with the nitrating agent ($N_2O_4$ or $NO_2$), resembles the reactants and attack occurs at the greatest rate from the more accessible (i.e., *cis*) direction.[362]

**Scope and Limitations.** There are no apparent restrictions on the nature of the olefin which can react with dinitrogen tetroxide to give dinitro adducts and nitro-nitrites. Additions to terminal and internal acyclic olefins, polyhaloethylenes, cyclic olefins, conjugated olefins (e.g., styrene and butadiene), and α,β-unsaturated esters, among others, have been recorded. In reaction with fluoroethylenes, only the dinitro adducts have been reported.[364,365] Under forcing conditions, it has been possible to form tetranitroalkanes by the addition of dinitrogen tetroxide to 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene.[366] While additions to disubstituted acetylenes proceed readily, additions to terminal acetylenes are not useful because of the unstable nature of the reaction mixtures.[367–369]

The use of oxygen as a carrier gas for the dinitrogen tetroxide affects the course of the reaction in various ways, according to the olefin being nitrated. With simple terminal alkenes, oxygen prevents reduction of dinitrogen tetroxide to dinitrogen trioxide,[362,364] and thereby permits a cleaner product mixture to be obtained. The only other apparent effect of the oxygen is to increase the amount of nitro-nitrate at the expense of

[362] Gardikes, Pagano, and Shechter, *J Am. Chem Soc*, **81**, 5420 (1959), *Chem & Ind.* (London), 1958, 632

[363] Stevens, *J Am Chem Soc*, **81**, 3593 (1959)

[364] Coffman, Raasch, Rigby, Barrick, and Hanford, *J Org. Chem*, **14**, 747 (1949)

[365] Haszeldine, *J Chem Soc*, 1953, 2075

[366] Grabiel, Bургове, and Clapp, *J Am. Chem Soc*, **77**, 1293 (1955)

[367] Campbell, Shavel, and Campbell, *J Am. Chem. Soc*, **75**, 2400 (1953)

[368] Schlubach and Rott, *Ann*, **594**, 59 (1955)

[369] Freeman and Emmons, *J Am Chem Soc*, **79**, 1712 (1957)

nitro-nitrite. However, with a number of other olefins including camphene,[370] allybenzene,[371] stilbene,[363] and styrene,[359] the use of tetroxide and oxygen mixtures results in the formation of products different from those obtained in the absence of oxygen. Stilbene reacts with dinitrogen tetroxide in ether, in the *absence* of oxygen to give, after hydrolysis, a mixture of 1,2-dinitro-1,2-diphenylethane (53%) and 1-hydroxy-2-nitro-1,2-diphenylethane (23%). In the *presence* of oxygen, no dinitro adduct is found, but there are obtained a 25% yield of 1-nitro-2-nitrato-1,2-diphenylethane and a 24% yield of $\alpha$-nitro-$\alpha$-phenylacetophenone along with about 30% of 1-hydroxy-2-nitro-1,2-diphenylethane.[363] Similar results are observed with the other olefins mentioned. It has been suggested that the effect of the oxygen in these instances may be due to its reaction with the relatively stable intermediate nitroalkyl radicals to give $\alpha$-nitroperoxy radicals or $\alpha$-nitroperoxynitrates.[359,363]

The addition of dinitrogen tetroxide to diethyl maleate, with or without solvent, is reported to give both the bis-nitrite and the nitro-nitrite.[372] The formation of the bis-nitrite was inferred from the isolation of tartaric acid on hydrolysis. This is the only report of the formation of a bis-nitrite.

Undecylenic acid is claimed to give the 10-nitro-11-nitrito adduct instead of the expected 11-nitro-10-nitrito compound.[373] This appears to warrant further investigation.

**Experimental Conditions.** The conditions worked out by Levy and co-workers[352-354] for the reaction of olefins with dinitrogen tetroxide and the isolation of the products involve the use of pure tetroxide, conversion of the unstable nitro-nitrite to the stable nitro alcohol prior to isolation, and the use of ether or ester-type solvents which reduce the oxidizing activity of the dinitrogen tetroxide. These conditions, which overcame many of the difficulties encountered by earlier workers, have been widely adopted. Maintaining the temperature below about 25° is usually essential, and interference by dinitrogen trioxide (easily formed from dinitrogen tetroxide) can be prevented by adding a small amount of oxygen along with the dinitrogen tetroxide.

In general, the olefins are added slowly to pure dry dinitrogen tetroxide or preferably to a concentrated solution of dinitrogen tetroxide in ether or ester-type solvents at −10° to +25°. Under these conditions, addition of tetroxide to the double bond occurs to give only the dinitroalkane and

[370] Stevens, *Chem. & Ind. (London)*, 1957, 1546.

[371] Stevens, *Chem. & Ind. (London)*, 1960, 499.

[372] Vasil'ev and Mikerin, *Sb. Statei Obsch. Khim., Akad. Nauk SSSR*, 1, 305 (1953) [*C.A.*, 49, 867 (1955)].

[373] Vasil'ev, *J. Gen. Chem. USSR (Engl. Transl.)*, 26, 819 (1956).

the nitro-nitrite. Some oxidation of the latter to nitro-nitrate occurs in the presence of oxygen. It is essential to convert the very unstable nitronitrite to a nitro alcohol by treatment with cold water or methanol, before attempting the isolation of the products. Failure to do so almost invariably results in violent decomposition of the reaction mixture when the solvent is removed.

The choice of solvent is rather critical. The best solvents are ethers, such as dioxane, diethyl ether, methylal, tetrahydrofuran, and tetrahydropyran, or acetate esters, all of which form molecular addition compounds with dinitrogen tetroxide. Substituted ethers, with reduced electron availability at the oxygen atom (e.g., 2,2'-dichlorodiethyl ether), do not form molecular complexes with dinitrogen tetroxide[374] and are found to be ineffective as solvents for its reaction with olefins.[352] The same thing can be said for hydrocarbons and chlorinated alkanes, although the latter have been used in the reaction of olefins with dinitrogen tetroxide/halogen mixtures.[375] While low temperatures and the use of an appropriate solvent are the normal conditions for successful reaction with most olefins, far more vigorous conditions are used with polyhalogenated olefins. Thus, in the formation of the dinitro adducts from chlorotrifluoroethylene, dichlorodifluoroethylene, and tetrafluoroethylene, mixtures of the olefin and dinitrogen tetroxide were heated in sealed vessels for several hours at 65° 365.

The importance of peroxide-free olefins has been stressed by Levy for the addition to cyclohexene.[376] The order of mixing the reagents affects the relative proportions of the products to some extent. Slow addition of cyclohexene to an excess of tetroxide at low temperature gave 42% dinitrocyclohexane, 25% nitrocyclohexanol, and 18% nitrocyclohexyl nitrate, while addition of tetroxide slowly to a cyclohexene-ether solution gave the same products in amounts of 30%, 54%, and 2%, respectively.

## Nitryl Chloride and Dinitrogen Tetroxide-Halogen Mixtures

**Mechanism.** The postulation of a free-radical chain mechanism for the addition of nitryl chloride to olefins[377] receives support from the following observations (1) The orientation of addition is the same to both electronegatively and electropositively substituted olefins. Terminal olefins and the addition of a nitro group is observed with vinyl bromide (to give 1-bromo-1-chloro-2 nitroethane), with propylene and other terminal olefins, and with acrylonitrile, methyl acrylate, and acrylic

[374] Rubin, Sisler, and Shechter, *J. Am. Chem. Soc.*, **74**, 877 (1952)
[375] Bachman, Logan, Hill, and Standish, *J. Org. Chem.*, **25**, 1312 (1960)
[376] Baldock, Levy, and Scaife, *J. Chem. Soc.*, 1949, 2627
[377] Shechter, Conrad, Daulton, and Kaplan, *J. Am. Chem. Soc.*, **74**, 3052 (1952)

acid. (2) In reaction with methyl acrylate, a 2:1 telomer, of structure $O_2NCH_2CH(CO_2CH_3)CH_2CHClCO_2CH_3$, has been isolated along with the 1:1 adduct.[377] (3) The products obtained in the reaction of nitryl chloride with cyclohexene are most readily explained by a free radical mechanism.[358]

The principal products from the nitryl chloride-cyclohexene reaction are 1-chloro-2-nitrocyclohexane and *trans*-1,2-dichlorocyclohexane, together with 2-chlorocyclohexanol and 2-chlorocyclohexyl nitrate (both deriving from 2-chlorocyclohexyl nitrite), and 2-nitrocyclohexanol (deriving from 2-nitrocyclohexyl nitrite). These products are in agreement with a mechanism wherein initiation occurs mainly by addition of $\cdot NO_2$ to the double bond followed by transfer with nitryl chloride in either of two ways.
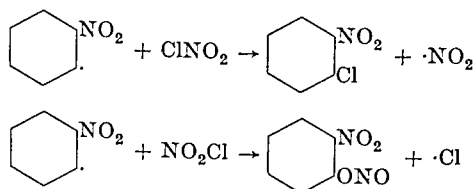


The formation of 2-chlorocyclohexyl nitrite indicates that some initiation must occur by chlorine atom addition, followed by transfer on nitryl chloride because initial attack by $\cdot NO_2$ always involves formation of a carbon-to-nitrogen rather than a carbon-to-oxygen bond. The formation of dichlorocyclohexane could be due to initiation by chlorine atom attack with subsequent transfer. However, the dichloro compound might also be formed by normal heterolytic addition of molecular chlorine which could arise by reaction of chlorine atoms with nitryl chloride. This process is

$$Cl\cdot + ClNO_2 \rightarrow Cl_2 + \cdot NO_2$$
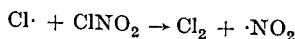
known to be important in the high-temperature decomposition of nitryl chloride.

It has recently been suggested that, whereas nitryl chloride adds by a free radical mechanism to double bonds with electron-withdrawing substituents, it may add ionically as $NO_2^+Cl^-$ to double bonds with electron-supplying groups.[375] However, such an assumption does not appear to be required in order to explain all the presently known cases of addition.

Closely related to nitryl chloride additions are the reactions of olefins with dinitrogen tetroxide/halogen mixtures. The isolation of $\beta$-iodonitroalkanes in high yield as products of the reaction of dinitrogen tetroxide

with olefins in the presence of iodine has been used as evidence for the free radical nature of the dinitrogen tetroxide/olefin reaction [300]  However, recent studies have shown that, whereas haloethylenes and other olefins containing electronegative substituents react with $N_2O_4/X_2$ mixtures ($X_2 = Br_2$ or $I_2$) to give $\beta$-halonitroalkanes, other olefins such as ethylene, propylene, and 1-butene, under conditions reactions conditions, give only 1-haloalkyl-2-nitrates [375,378]  The latter products are undoubtedly formed by an ionic reaction  It thus appears that $N_2O_4/X_2$ mixtures can react with simple non-electronegatively substituted olefins, to give either $\beta$-halonitro compounds or 1-haloalkyl-2-nitrates by what are probably competing free radical and ionic reactions and that the product formed is determined by the conditions chosen for the reaction (see "Experimental Conditions," p 232)  Of interest, also, is the fact that in the vapor phase at 260–275° the reaction of propylene or of 1-butene with $N_2O_4/Cl_2$ gives rise to the 1-chloro-2-nitroalkanes along with major amounts of dichloroalkanes.  This reaction no doubt is initiated by addition of a chlorine atom.  In the liquid phase, only dichloroalkanes are formed

**Scope and Limitations.**  The addition of nitryl chloride to olefins is apparently general, and no limitations with respect to the nature of the olefin have been noted.  There is, however, considerable variation in reactivity of olefins with this reagent  For example, the reaction with vinyl bromide becomes violent at slightly elevated temperatures, while reactions with dichloro-, trichloro-, and tetrachloro-ethylene have been effected at 100° without a solvent. [379]  Generally such vigorous conditions are neither necessary nor desirable.  The principal product is the nitrochloroalkane, often mixed with smaller amounts of various other adducts, as illustrated above with cyclohexene.

The structure of the nitrochloroalkane can generally be predicted by assuming attack of the $\cdot NO_2$ radical on the least substituted carbon atom of the double bond followed by transfer of nitryl chloride  However, other products can arise, apparently as a result of initial attack by a chlorine atom followed by transfer on the nitryl chloride  Thus the structures expected for the reaction products from styrene[379] and from cinnamic acid,[379] viz , $\alpha$-nitro-$\beta$-chloroethylbenzene and $\alpha$-chloro-$\beta$-nitro-$\beta$-phenylpropionic acid, respectively could be rationalized on the basis of such a mechanism predominating  More study of this possibility seems called for, especially in view of the importance of an analogous chain mechanism in sulfenyl halide additions  (See p 204 )

There has been little study of the reaction of nitryl chloride with acetylenes.  The reaction with phenylacetylene was originally reported to

[378] Bachmann and Logan, *J. Org Chem* , **21**, 1467 (1956)
[379] Steinkopf and Kuhnel, *Ber* , **75**, 1323 (1942). Belg pat 443,701 [*C A* , **42**, 201 (1948)].

yield α-nitro-β-chlorostyrene,[379] but recent work indicates that the major constituent of the "difficulty separable mixture of products" is α-chloro-β-nitrostyrene.[369] The only other acetylene to be treated with nitryl chloride is dichloroacetylene reported, without details, to give trichloronitroethylene.[380]

The principal point to be considered with respect to reactions of dinitrogen tetroxide/halogen mixtures with olefins is the possible competition between the ionic reaction leading to halonitrates[378] and the free radical reaction leading to halonitroalkanes.[360,375] This is discussed more fully under "Experimental Conditions" below. The free radical reaction has been demonstrated for a moderate number of olefins and for a few acetylenes. With electronegatively substituted olefins, there is no interference from the ionic reaction under any of the conditions studied, but considerable amounts of the *vic*-dihaloalkanes are obtained when mixtures of dinitrogen tetroxide with either chlorine or bromine are used. With iodine, this is not a serious matter, and 50–90% yields of the iodonitroalkanes are easily obtained. The rate of reaction of halogenated ethylenes decreases with increasing number of halogen atoms in the olefins.[375] No adduct is obtained with tetrachloroethylene in 72 hours.

With propylene and 1-butene, only dichloroalkanes are obtained in liquid-phase reactions with dinitrogen tetroxide-chlorine mixtures.[381]

**Experimental Conditions.** The conditions used in effecting addition of nitryl chloride to olefins cover a rather wide range. Solvents are generally employed but apparently are not essential in most instances. Among the more effective solvents are chlorinated hydrocarbons, nitromethane, difluorodichloromethane, and diethyl ether. Paraffin-type solvents are less satisfactory and give lower yields.[382]

In reaction with isobutylene, a 51% yield of adduct is obtained in the absence of a solvent, a 20% yield in pentane, and a 64% yield in chloroform.[382]

An unusual influence of solvent on product mixture is found with acrylonitrile. In the absence of solvent, a 76% yield of α-chloro-β-nitropropionitrile is obtained, while in the presence of diethyl ether this product is obtained in only 25% yield together with β-nitroacrylonitrile in 48% yield.[377]

The reaction temperatures, in either the presence or absence of solvent, vary mostly between about −20° and +20°. The reaction with chlorinated ethylenes appears to require far more vigorous conditions. For example, trichloroethylene is heated in a bomb at 100° for 3 hours to

[380] Brintzinger and Pfannstiel, *Z. Anorg. Chem.*, **255**, 325 (1948).
[381] Bachman and Chupp, *J. Org. Chem.*, **21**, 465 (1956).
[382] Himel, U.S. pat. 2,511,915 [*C.A.*, **44**, 8360 (1950)].

obtain a 70% yield of adduct [383]  By contrast, vinyl bromide reacts so rapidly with nitryl chloride that cooling of the reaction mixture is essential [379]

The reaction of olefins with mixtures of dinitrogen tetroxide and halogen has been shown to proceed in the vapor phase[381] as well as in the liquid phase [360,375]  Propylene and 1-butene react with dinitrogen tetroxide-chlorine mixtures at 260–275° and a contact time of a few seconds to give low yields of the respective 1-chloro-2-nitroalkanes together with major amounts of the dichloroalkane  In the liquid phase at about 0°, only dichloroalkanes are formed [381]  When bromine or iodine is used instead of chlorine, in the liquid phase, $\beta$-haloalkyl nitrates are obtained from ethylene and its simple homologs [365]  The conditions used involve the addition of the olefin to a chloroform or carbon tetrachloride solution of dinitrogen tetroxide and halogen, at about 0° [378]  Under identical conditions, electronegatively substituted olefins, especially the haloethylenes, react with dinitrogen tetroxide-halogen mixtures (even where $X_2 = Cl_2$) to give the $\beta$-halonitroalkanes [365]  Thus, under this particular set of conditions, the nature of the product is apparently determined by the structure of the olefin  However, if a stream of dinitrogen tetroxide in nitrogen is passed slowly into an ether solution of an olefin and excess iodine, the products are invariably the $\beta$-iodonitroalkanes [360]  This is true for a wide variety of olefins, and, although it has not been reported, it may be presumed that bromine could be substituted for iodine in this scheme to obtain $\beta$-bromonitroalkanes.

## EXPERIMENTAL PROCEDURES

*cis*-1-Bromo-2-chlorocyclohexane (Addition of Hydrogen Bromide to 1-Chlorocyclohexene).[26,27]  A solution of 10 g. (0.085 mole) of 1-chlorocyclohexene in 265 g  (3 7 moles) of pentane is placed in a quartz flask fitted with a condenser, a fritted glass gas bubbler, and a magnetic stirrer.  The flask is partially immersed in ice water and is irradiated with a Hanovia-S-100 quartz tube mercury vapor lamp for 2 hours while hydrogen bromide is passed through the solution  The dried pentane solution, after washing with 10% aqueous sodium carbonate and water, is distilled, to give crude cis-1-bromo-2-chlorocyclohexane (b p  91–97°/10 mm,  –11° to –8°) in 88% yield.  The crude product, which contains less than 0 4% of the *trans* isomer, is further purified by recrystallization from pure pentane, followed by fractional distillation to give pure *cis*-1-bromo-2-chlorocyclohexane, b p. 87 5–88°/7 mm ,  $n_D^{25}$ 1 5238.

[383] Kuhnel, Ger pat  739,633 [C A , 40, 347 (1945)]

**1-Bromo-1-hexene (Addition of Hydrogen Bromide to *n*-Butylacetylene in the Presence of Peroxides).**[35] One mole (82 g.) of *n*-butylacetylene, containing about 0.8 mole % of peroxide, is placed in a 500-ml. three-necked flask equipped with a stirrer, an inlet tube, and a reflux condenser. The flask is cooled in an ice bath, and 1.5 moles of dry hydrogen bromide is passed in rapidly. At the end of 1 hour the reaction mixture is washed with aqueous sodium carbonate followed by water, and dried over anhydrous sodium sulfate. Distillation through an efficient column gives 5 g. of unreacted *n*-butylacetylene, 120 g. (74%) of 1-bromo-1-hexene (b.p. 139–141°/751 mm.; $n_D^{20}$ 1.4596), and 3 g. of 1,2-dibromohexane (b.p. 89–90°/19 mm.; $n_D^{20}$ 1.5024).

When 2.0 moles of hydrogen bromide is passed into 1 mole of *n*-butylacetylene containing 0.6 mole % of peroxides, during 3 hours at ice-bath temperature, the product consists of 85 g. (37%) of 1-bromo-1-hexene and 91 g. (52%) of 1,2-dibromohexane.

**Trifluoromethyl 2,2-Difluoroethyl Sulfide (X-Ray-Initiated Addition of Trifluoromethanethiol to 1,1-Difluoroethylene).**[6] A mixture of 27 g. (0.275 mole) of trifluoromethanethiol and 14 g. (0.218 mole) of 1,1-difluoroethylene is loaded into a 100-ml. stainless steel pressure vessel, and the mixture is irradiated with x-rays for 3 hours at an average dose rate of ca. 16,000 rad./min.* Volatiles are bled off and the residue is distilled through a small spinning-band still. There is obtained 26 g. (72%) of trifluoromethyl 2,2-difluoroethyl sulfide distilling at 55–58° (mostly 58°); $n_D^{25}$ 1.3270–1.3276.

**3-(2-Methyl)pentyl Thiolacetate (UV-Initiated Addition of Thiolacetic Acid to 2-Methyl-2-pentene).**[384] Freshly distilled thiolacetic acid (152.2 g., 2 moles) is added slowly with stirring to 336.6 g. (4 moles) of 2-methyl-2-pentene. The reaction mixture is irradiated during the addition with a 100-watt bulb, and irradiation and stirring are continued for an hour after the addition is complete. Distillation of the reaction mixture yields 309 g. (96%) of 3-(2-methyl)pentyl thiolacetate; b.p. 70°/13 mm.; $n_D^{25}$ 1.4603.

**3-Acetoxyprop-1-enyl Thiolacetate and 2,3-*bis*-(Acetylthio)propyl Acetate (Addition of Thiolacetic Acid to Propargyl Acetate).**[174] A mixture of 7.4 g. (0.075 mole) of propargyl acetate, 11.4 g. (0.15 mole) of thiolacetic acid, and 0.1 g. of α,α′-azo-bis(isobutyronitrile) contained in a sealed glass tube is irradiated for 24 hours with a 200-watt mercury lamp. Distillation of the reaction mixture yields 1.5 g. (10%) of

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* The x-rays were generated by impinging 3-Mev. electrons from a Van de Graaff accelerator on a water-cooled gold target mounted beneath the window of the electron tube. Dose rates were determined by ferrous sulfate dosimetry.

[384] Bordwell and Hewett, *J. Org. Chem.*, **22**, 980 (1957).

3-acetoxyprop-1-enyl thiolacetate (b.p. 95–97°/3 mm ; $n_D^{15}$ 1·5115) and 12·0 g. (65%) of 2,3-bis(acetylthio)propyl acetate (b.p. 92–95°/0·01 mm ; $n_D^{15}$ 1·5181)

## 2-Phenoxyethanethiol and bis-(2-Phenoxyethyl) Sulfide (Addition of Hydrogen Sulfide to Vinyl Phenyl Ether).[200] A mixture of 20 g. (0·166 mole) of vinyl phenyl ether, 12 g. (0·352 mole) of hydrogen sulfide, and 0·04 g. of α,α'-azo-bis(isobutyronitrile) is sealed under vacuum in a glass tube. After 16 days, including 53 hours at 60°, the tube is opened. Upon distillation of the reaction mixture there is obtained 16 g. (62%) of 2-phenoxyethanethiol distilling at 96–100°/4–4·5 mm ; $n_D^{20}$ 1·5600. The residue (7·2 g., 32%) is recrystallized from alcohol to yield bis-(2-phenoxyethyl) sulfide melting at 54·5–55°.

## Sodium 1,1,2,3,3,3-Hexafluoropropane-1-sulfonate (Addition of Sodium Bisulfite to Hexafluoropropene).[215] A mixture of 90 g. (0·6 mole) of hexafluoropropene, 60 g. (0·5 mole) of sodium bisulfite, 27·4 g. of borax, 120 ml. of water, and 0·8 g. of benzoyl peroxide is charged into a stainless steel autoclave. The contents of the autoclave are heated with agitation at 110–120° for 9 hours. The reaction mixture is evaporated to dryness and the residue extracted with hot ethanol. Upon evaporation of the ethanol there is isolated about 115 g. (91%) of crude sodium 1,1,2,3,3,3-hexafluoropropane-1-sulfonate.

## p-Chlorophenyl 2-Chloroethyl Sulfone (Addition of p-Chlorobenzenesulfonyl Chloride to Ethylene).[229] A mixture of 315 g. (0·67 mole) of p-chlorobenzenesulfonyl chloride and 12·3 g. of α,α'-azo-bis-(isobutyronitrile) is loaded into a 1250-ml. autoclave. The autoclave is evacuated and ethylene admitted until a pressure of 1500 p.s.i. is attained at 70°. The autoclave is agitated for 24 hours at 70°, the initial pressure being maintained by addition of ethylene, and then vented. The reaction mixture is distilled to yield 74 g. (21%) of crude p-chlorophenyl 2-chloroethyl sulfone distilling at 134–163°/0·4–0·6 mm. and 127 g. (32%) of material boiling in the range 168–184°/0·6–0·8 mm., which is chiefly p-chlorophenyl 4-chlorobutyl sulfone.

## n-Octyltrichlorosilane (Addition of Trichlorosilane to 1-Octene).[256] A mixture of 17·9 g. (0·16 mole) of 1-octene and 135·5 g. (1·0 mole) of trichlorosilane (b.p. 32°) is placed in a flask fitted with dropping funnel, thermometer, and reflux condenser connected through a −80° trap to a mercury seal 20 cm. in height. The system is swept with nitrogen and the reaction mixture heated to 45° under the slight extra pressure of the mercury. A solution of 3 g. (0·025 mole) of diacetyl peroxide in 19·9 g. (0·17 mole) of 1-octene is added during 2 hours, after which the mixture is heated at 50–63° for an additional 9 hours. Distillation under reduced pressure gives, after removal of excess trichlorosilane,

80.9 g. (99%) of *n*-octyltrichlorosilane, which boils at 231–232°/728 mm. on subsequent redistillation.

**Methyl-*n*-propyldichlorosilane (Thermal Addition of Methyldichlorosilane to Propylene).**[258] A mixture of 345 g. (3 moles) of methyldichlorosilane and 128 g. (3 moles) of propylene in a 2.4-l. pressure bomb is heated overnight at 300°. The maximum pressure is 1120 p.s.i. Distillation of the reaction mixture gives 340 g. (72%) of methyl *n*-propyldichlorosilane, boiling at 123-124°/747 mm. Some methylhexyldichlorosilane was formed in the reaction.

**Diethyl β-Acetoxypropyl Phosphonate (Peroxide-Initiated Addition of Diethyl Phosphite to Isopropenyl Acetate).**[333] A solution of 5 g. of benzoyl peroxide in 93 g. (0.93 mole) of isopropenyl acetate is added during 3 hours to 319 g. (2.30 moles) of diethyl phosphite held at 85–95°. When the addition is complete, an additional 5 g. of benzoyl peroxide is added and heating is continued for another hour. After removal of the excess diethyl phosphite under reduced pressure, the residual oil is distilled. The fraction boiling at 78–100°/0.50 mm yields on redistillation 160 g. (72%) of diethyl β-acetoxypropyl phosphonate, b.p. 89–93°/0.05 mm., $n_D^{25}$ 1.4301.

Fractionation of the higher-boiling fractions yields about 25 g. of a substance containing 2 units of isopropenyl acetate to 1 of diethyl phosphite, b.p. 100–115°/0.01 mm., $n_D^{25}$ 1.4461.

**1-Nitro-2-propyl Iodide (Addition of Dinitrogen Tetroxide to Propylene).**[360] Dinitrogen tetroxide (6.9 g.; 0.15 mole as $NO_2$) in a stream of dry nitrogen is passed into a cold (0°) stirred solution of 30 ml. of propylene and 31 g. (0.25 mole) of iodine in 200 ml. of diethyl ether during 2 hours. The reaction system is protected by a solid carbon dioxide-acetone condenser and a drying tube. Stirring is continued for 1 hour at 0° after the addition of the dinitrogen tetroxide. The ether solution is washed with 15% aqueous sodium thiosulfate until colorless, then with aqueous sodium bicarbonate and water, and dried over magnesium sulfate. The residue remaining after evaporation of the ether at 30 mm. pressure is distilled through a brown glass distilling head to give 22.5 g. (70%) of 1-nitro-2-propyl iodide, b.p. 40–42°/0.5 mm. Redistillation gives 1.7 g. of fore-run (b.p. 42–44°/0.45 mm.; $n_D^{20}$ 1.5370) and 18.4 g of 1-nitro-2-propyl iodide (b.p. 44°/0.45 mm., $n_D^{20}$ 1.5378).

**2-Chloro-3-nitropropionic Acid (Reaction of Nitryl Chloride with Acrylic Acid).**[377] Nitryl chloride (85 g., 1.05 mole; 20% excess) is distilled through a gas delivery tube into 64 g. (0.89 mole) of glacial acrylic acid at 0°. The orange-red mixture is stirred at room temperature for an hour, and excess nitryl chloride is then removed under reduced pressure. The syrupy product crystallizes slowly at 0–5° to a white solid

(109 g., 71%). A 20-g. sample of this material is dissolved in benzene, the solution separated from an insoluble residue (1 5 g) and concentrated until precipitation occurs Filtration gives a white solid (11 4 g.), m p. 72–74°, which when recrystallized from benzene yields 2-chloro-3-nitropropionic acid, m.p 78–80°.

Distillation of the crude reaction product at 0 7 mm pressure results in dehydrochlorination of the 2-chloro-3-nitropropionic acid to 3-nitroacrylic acid, m.p 136°.

**1,2-Dinitro-2,4,4-trimethylpentane and 1-Nitro-2,4,4-trimethyl-2-pentanol (Addition of Dinitrogen Tetroxide to 2,4,4-Trimethyl-1-pentene).**[378] 2,4,4-Trimethyl-1-pentene (332 g.) is added dropwise during 3 hours to a well-stirred solution of 790 g. of dinitrogen tetroxide in 1830 g of dry diethyl ether at −5°. Solvent and excess tetroxide are then removed, and the product, a yellow oil, is stirred with two 600-ml. portions of water for 20 minutes to hydrolyze the nitro-nitrite After the oil has stood with water overnight, it is separated and dried by azeotropic distillation with benzene. Fractional distillation of the dried oil (610 g) gives (i) 169 g., b p 52–68°/0.5 mm , (ii) 339 g , b p 80–130°/<1 mm , and (iii) a residue of 54 g

Redistillation of (i) gives 163 g. (31%) of 1-nitro-2,4,4-trimethyl-2-pentanol, b p. 58–62°/<1 mm.

Redistillation of fraction (ii) gives a center cut of 320 g. (53%) of 1,2-dinitro-2,4,4-trimethylpentane, b p. 94–102°/<1 mm

## TABULAR SURVEY

The unsaturates are tabulated according to increasing number of carbon atoms following the system used in *Chemical Abstracts*. Where necessary, the addends have also been arranged according to increasing number of carbon atoms. The silanes in Table XI-C and the phosphines in Table XIII have been arranged in order of decreasing number of hydrogen atoms on the hetero atom

A dash in the yield column indicates that no yield was reported.

The literature survey included *Chemical Abstracts* index through 1960. Although no exhaustive search of the 1961–early 1962 literature was possible, all the papers encountered in the readily available journals are included.

## TABLE IX

### HYDROHALOGENATIONS

*A. Addition of Hydrogen Bromide to Olefins*

| Olefin | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| $CF_2=CFCl$ | UV | $CF_2BrCHFCl$ (88) | 385 |
| $CF_2=CF_2$ | UV | $CF_2BrCHF_2$ (66) | 385 |
| $CCl_2=CHCl$ (+ DBr) | Peroxide (UV) | $CDCl_2CHClBr$ (nearly quant.) | 386 |
| $CCl_2=CHCl$ | Peroxide | $CHCl_2CHClBr$ (90) | 58 |
| $CF_2=CHCl$ | UV | $CF_2BrCH_2Cl$ (99) | 4 |
| $CF_2=CHF$ | UV | $CHF_2CHFBr$ (57) | 5 |
| | | $CF_2BrCH_2F$ (43) | |
| $CCl_2=CH_2$ (+ DBr) | UV | $CDCl_2CH_2Br$ (64) | 22 |
| | | $CDCl_2CH_2CCl_2CH_2Br$ | |
| $CCl_2=CH_2$ | UV | $CHCl_2CH_2Br$ (62) | 22 |
| | | $CHCl_2CH_2CCl_2CH_2Br$ (32) | |
| $CF_2=CH_2$ | UV | $CHF_2CH_2Br$ (85) | 387 |
| $CHBr=CH_2$ (+ DBr) | None added | $CH_2BrCH_2Br$ (92) | 388 |
| $CDBr=CH_2$ (+ DBr) | Light | $CHDBrCH_2Br$ (—) | 389 |
| $CHBr=CD_2$ | Light | $CD_2BrCH_2Br$ (—) | 389 |
| $CDBr=CD_2$ | Light | $CH_2BrCD_2Br$ (—) | 389 |
| $CHCl=CH_2$ | Light | $CHDBrCD_2Br$ (—) | 389 |
| | Peroxide | $CH_2ClCH_2Br$ (79) | 390 |
| | UV | $CH_2ClCH_2Br$ (68) | 391 |
| $CF_3CF=CF_2$ | Light | $CF_3CHFCF_2Br$ (88) | 392 |
| | X-rays or UV | $CF_3CHFCF_2Br$ (47) | 44 |
| $CF_3CH=CF_2$ | UV | $CF_3CFBrCHF_2$ (29) | 393 |
| $CCl_3CCl=CH_2$ | Peroxide | $CF_3CH_2CF_2Br$ (40) | 52 |
| | | $CHCl_2CCl_2CH_2Br$ (ca. 30) | |
| | | $CCl_2=CClCH_2Br$ | |

| Olefin | Conditions | Product | References |
|---|---|---|---|
| CCl₃CH=CH₂ | Peroxide | $CHCl_2CHClCH_2Br$ (77) | 50 |
| CHCl₂CCl=CH₂ | Peroxide | $CHCl_2CHClCH_2Br$ (ca. 20) | 52 |
| CFCl₂CH=CH₂ | UV | $CFCl_2CH_2CH_2Br$ (38) | 57 |
| | UV | $CHFClCHClCH_2Br$ (18) | 394, 395 |
| CF₃CH=CH₂ | Peroxide | $CF_3CH_2CH_2Br$ (90–97) | 55, 66 |
| | | $CHCl_2CH_2CH_2Br$ (5) | 42 |
| CHCl₂CH=CH₂ | | $CH_2ClCHClCH_2Br$ (45) | 12 |
| | | $CH_3CHClCH_2CH_2Br$ (93) | 61, 16 |
| | | $CF_3CH_2CH_2I$ (90) | 29 |
| CH₃CH=CF₂ | Oxygen | $CH_2BrCH_2CH_2Br$ (90) | 11 |
| CH₂BrCH=CH₂ | Ni or Fe | $CH_2BrCH_2CH_2Br$ (37–28) | 9 |
| | | $CH_2BrCHClCH_2Br$ (2–3) | 9 |
| | Oxygen | $CH_2BrCH_2CH_2Br$ (20–60) | 9 |
| | | $CH_2BrCHClCH_3$ (85) | |
| CH₂CBr=CH₂ | | $CH_2CBr_2CH_3$ (14) | 37 |
| | Peroxide | $CH_2ClCHClCH_2Br$ (84) | 396, 397 |
| CH₃CH=CHBr | Peroxide | $CH_3CHClCH_2Br$ (74) | |
| CH₃CCl=CH₂ | | $CH_3CCl_2CCl_3$ (28) | |
| CH₃CH=ClCl | | $CH_3CHBrCH_2Cl$ (99) | |
| Cl₃SiCH₂CH=CH₂ | Peroxide | $Cl_3SiCH_2CH_2Cl$ (87) | |
| CH₃CH=CH₂ | Peroxide | $CH_3CH_2CH_2Br$ (78) | |
| | | $CH_3CHBrCH_3$ (12) | |
| | Bromoacetone | $CH_2ClCH_2Br$ (quant.) | 13, 398 |
| | UV | $CH_3CH_2CH_2Br$ (quant.) | 391, 11 |
| | $(C_2H_5)_4Pb$ + light | $CH_3CH_2CH_2Br$ (60) | 60, 11 |
| | Silent discharge | $CH_3CH_2CH_2Br$ (98) | 399, 14 |
| CF₃CF=CFCF₃ | UV | $CF_3CHFCF_2CF_3$ (60) | 387 |
| CF₂CF=CF₂ | UV | $CF_2CHFCFBrCF_3$ (33) | 387 |

Note. References 385 to 631 are on pp. 371–376.

TABLE IX—Continued

A. Addition of Hydrogen Bromide to Olefins—Continued

| Olefin | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| (CF₃)₂C=CH₂ | UV | (CF₃)₂CHCH₂Br (93) | 42 |
| CH₂ClBr=CHCH₂ | UV | CH₂ClBrCHBrCH₂, cis (72); trans (18) | 28 |
| CCl₃C(CH₃)=CH₂ | Peroxide | CHCl₂CCl(CH₃)CH₂Br (—); Cl₂C=C(CH₃)CH₂Br (—) | 51 |
| CH₃CCl₂CH=CH₂ | Peroxide | CH₃CHClCHClCH₂Br (73) | 55 |
| CHCl₂C(CH₃)=CH₂ | Peroxide | CHCl₂CH(CH₃)CH₂Br (34); CH₂ClClCl(CH₃)CH₂Br (30) | 55, 53 |
| CH₂=CHCH=CH₂ | Peroxide | CH₃CH=CHCH₂Br (44–76); CH₂=CHCHBrCH₃ (56–24) | 400 |
| CH₃CH=CHCO₂H | * | CH₃CHBrCH₂CO₂H | 401, 402 |
| CH₃CHBrCH=CH₂ | Peroxide | CH₃CHBrCH₂CH₂Br (83) | 400 |
| CH₂BrCH=CHCH₃ | Peroxide | CH₃CHBrCHBrCH₃ (17); CH₂BrCH₂CHBrCH₃ (78) | 400 |
| cis-CH₃CBr=CHCH₃ | UV | CH₃CHBrCHBrCH₃ (16); meso-CH₃CHBrCHBrCH₃ (92) | 403 |
| trans-CH₃CBr=CHCH₃ | UV | d,l-CH₃CHBrCHBrCH₃ (5); meso-CH₃CHBrCHBrCH₃ (9) | 403 |
| CH₃CH₂CH=CH₂ | Peroxide | d,l-CH₃CHBrCHBrCH₃ (83) | 404 |
|  | UV | CH₃CH₂CH₂CH₂Br (95) | 11, 391 |
|  | Bromoacetone | CH₃CH₂CH₂CH₂Br (99) | 13, 398 |
|  | Silent discharge | CH₃CH₂CH₂CH₂Br (quant.); CH₃CH₂CH₂CH₂Br | 14 |

| Reactant | Conditions | Products | Reference |
|---|---|---|---|
| (CH₃)₂C=CH₂ | Peroxide | (CH₃)₂CHCl₂Br (91) | 403, 406 |
| cis-CH₃CH=CHCH₃ (+ DBr) | UV | (CH₃)₃CBrCl₂ (6) | 391 |
| trans CH₃CH=CHCH₃ (+ DBr) | Light | (CH₃)₂CHBrCH₂ | 23 |
| | Light | threo-CH₃CHXCHHrCH₃ (95) | 23 |
| CH₃(CH₂)₃SCH(CH₃)CH=CH₂ | Peroxide | erythro-CH₃CHBrCHBrCH₃ (quant.) | 37 |
| Cl₃SiCl(CH₂)₂CH=CH₂ | Peroxide | CH₃(CH₂)₃SCH(CH₃)CH₂CH₂Br (72) | 37 |
| (CF₃)₂C=CHCO₂H | Peroxide (UV) | Cl₃SiCl(CH₂)₄Br (85) | 407 |
| | | (CF₃)₂ClCHHCH₂H (97) | |
| [ring]—Br | UV | Br cis (91) / Br trans (6) | 25 |
| CH₂=CHCH₂CH₂CO₂H | Peroxide | CH₂BrCH(CH₂)₂CH₂CO₂H (80 100) | 408 |
| CH₂=C(CH₃)CO₂CH₃ | * | CH₂BrCH(CH₂)₂CO₂CH₃ (quant.) | 409 |
| CH₃CH₂SCH(CH₃)CH=CH₂ | * | CH₂BrC(CH₃)₂Br (96) | 410 |
| CH₃CH₂CH=CHCH₃ | Peroxide | CH₃CH(CH₂)₂CHBrCH₃ (36) | 411 |
| | | CH₃CH₂CHBrCH₂CH₃ (60) | |
| [cyclopentane] | Peroxide | (CH₃)₂CBrCH₂CH₃ (13 6) | 412 |
| (CH₃)₂C=CHCH₃ | Peroxide | (CH₃)₂CBrCH₂CH₃ (6 4) | 401, 62 |
| ClCH₂SCl(CH₃)₂=CH₂ | Peroxide | (CH₃)₂ClCBrCH₂CH₃ (24) | 37 |
| (CH₃)₂SiCl=CH₂ | Peroxide | ClCH₂SCl(CH₃)₂CHBrCH₃ (82) | 413 |
| | | (CH₃)₂SiCl₂CHBrCH₃ (79) | |
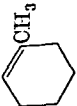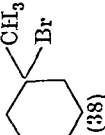
*Note* References 385 to 631 are on pp. 371–376.

* The same product was obtained with or without added peroxide.

TABLE IX—Continued

A. Addition of Hydrogen Bromide to Olefins—Continued

| Olefin | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| $CF_3CH=CHCO_2C_2H_5$ | * | $CF_3CHBrCH_2CO_2C_2H_5$ (—) | 414 |
|  | UV |  (76–81) cis | 26, 27 |
|  | UV or peroxide |  (73–88) cis | 27 |
| $CH_2=CH(CH_2)_2CH=CH_2$ | UV | $Br(CH_2)_6Br$ (quant.) | 11 |
| | None added | $CH_2Br(CH_2)_3CH=CH_2$ (21) | 415 |
| | | $CH_3CHBr(CH_2)_2CH=CH_2$ (26) | |
| $CH_3CH=CHCO_2C_2H_5$ | None added | $CH_3CHBrCH_2CO_2C_2H_5$ | 401 |
| $C_4H_9CBr=CH_2$ | Peroxide | $C_4H_9CHBrCH_2Br$ (84) | 35 |
| $CH_3(CH_2)_3CH=CH_2$ | Silent discharge | $CH_3(CH_2)_4CH_2Br$ (08) | 14 |
| $(CH_3)_3SiCH_2CH=CH_2$ | Peroxide | $(CH_3)_3SiCH_2CHBrCH_3$ (73) | 36 |
| $(CH_3)_3CCH_2CH=CH_2$ | Peroxide | $(CH_3)_3CCH_2CH_2CH_2Br$ ("High") | 416 |
|  | UV |  (50) +  (38) | 26 |

| | | | |
|---|---|---|---|
| $(C_2H_5)_2NCH_2CH=CH_2$ | Peroxide | $(C_2H_5)_2NCH_2CH_2CH_2CH_3$ (19)  $(C_2H_5)_2NCH_2CH_2CH_2Br$ (29) | 417  29 |
|  | UV |  | 29 |
|  | UV |  | 29 |
| $C_6H_5CH=CH_2$ | | | |
| $CH_3(CH_2)_2CH=CH_2$ | Peroxide | $C_6H_5CH_2CH_2Br$ (80) | 401 |
| $C_6H_5CH_2CH=CH_2$ | Peroxide | $C_6H_5CH_2CH_2Br$ (15) | 15 |
| $o\text{-}CH_3C_6H_4CH=CH_2$ | Peroxide | $CH_3(CH_2)_3CH_2CH_2Br$ (80) | 418 |
| $m\text{-}CH_3C_6H_4CH=CH_2$ | Peroxide | $o\text{-}CH_3C_6H_4CH_2CH_2CH_2Br$ (66) | 418 |
| $p\text{-}CH_3C_6H_4CH=CH_2$ | Peroxide | $m\text{-}CH_3C_6H_4CH_2CH_2CH_2Br$ (80) | 418 |
| $CH_3(CH_2)_4CH=CH_2$ | Peroxide | $p\text{-}CH_3C_6H_4CH_2CH_2CH_2Br$ (70) | 418 |
| $CH_3(CH_2)_4CH=CH_2$ | Peroxide | $p\text{-}CH_3C_6H_4CH_2CH_2CH_2CH_2Br$ (70) | 418 |
| $3,4\text{-}(CH_3)_2C_6H_4CH_2CH=CH_2$ | Peroxide | $CH_3(CH_2)_8CH_2Br$ (65) | 418, 410 |
| | Peroxide | $3,4\text{-}(CH_3)_2C_6H_4CH_2CH_2CH_2CH_2Br$ (35) | 15 |
| $CH=CH(CH_2)_{10}CO_2H$ | | $Br(CH_2)_{10}CO_2H$ (35) | 418 |
| | Ni | $CH_3CHBrCH(CH_2)_8CO_2H$ (85) | 420 |
| | | | 17, 18 |

Note: References 385 to 631 are on pp. 371–376.
* The same product was obtained with or without added peroxide.

TABLE IX—*Continued*

A. Addition of Hydrogen Bromide to Olefins—*Continued*

| Olefin | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| $CH_3CH$=$CH(CH_2)_7CO_2H$ | Peroxide | $CH_3CH_2CHBr(CH_2)_7CO_2H$ $\}$† | 421 |
| | | $CH_3CHBr(CH_2)_8CO_2H$ | |
| $CH_3(CH_2)_{10}CH$=$CH_2$ | Peroxide | $CH_3(CH_2)_{11}CH_2Br$ (85) | 15 |
| $CH_2$=$CH(CH_2)_8CO_2C_2H_5$ | Peroxide | $Br(CH_2)_{10}CO_2C_2H_5$ (80)‡ | 422 |
| $CH_2$=$CH(CH_2)_9OCOCH_3$ | Peroxide | $Br(CH_2)_{11}OCOCH_3$ (—) | 422 |
| $CH_3(CH_2)_{12}CH$=$CH_2$ | Peroxide | $CH_3(CH_2)_{13}CH_2Br$ (60) | 15 |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2H$ | UV | 9-Bromo-acid $\}$† | 423 |
| | | 10-Bromo-acid | |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2CH_3$ | UV | 9-Bromo ester $\}$† | 423 |
| | | 10-Bromo ester | |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2C_6H_5$ | Peroxide | 9-Bromo ester $\}$† | 423 |
| | | 10-Bromo ester | |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2C_6H_4NO_2$-$p$ | Peroxide | 9-Bromo ester $\}$† | 423 |
| | | 10-Bromo ester | |
| $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2C_6H_4OCH_3$-$p$ | Peroxide | 9-Bromo ester $\}$† | 423 |
| | | 10-Bromo ester | |

*B. Addition of Hydrogen Bromide to Acetylenes*

| Acetylene | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| DC≡CD | Light | CHD—CDBr (—) | 389 |
| | | CHDBrCHDBr (—) | |
| (+ DBr) | Light | CD₂=CDBr (—) | 389 |
| | | CD₂BrCD₂Br (—) | |
| (+ DBr) | UV | CD₂BrCHD₂ (—) | 424 |
| HC≡CH | Light | CH₂=CHBr (—) | 389 |
| | | CH₂BrCH₂Br (quant.) | |
| (+ DBr) | Light | CH₂=CHBr (—) | |
| | | CHD—CHBr (—) | |
| | | CHDBrCHDBr (—) | |
| CH₂=CBr | UV | CH₂CBr=CHBr (75% *trans*) (92) | 32 |
| CF₃C≡CH | UV | CF₃CH=CHBr (—) | 39 |
| HC≡CH | Peroxide | CH₂CHClCH₂Br (95–100) | 41 |
| | Light | *cis*-CH₂CH=CHBr (70) | 30 |
| | | CH₂CHBrCH₂Br (30) | |
| CF₃C≡CCF₃ | UV | CF₃CBr=CClCF₃ (87) | 39 |
| CH₂C≡CCH₃ | Peroxide | *d,l*-CH₃CHBrCHBrCH₃ (86) | 31 |
| | | CH₃CH₂CH₂CH₃ (4) | |
| | | *trans*-(CH₃)₂CCBr=CHBr (89) | 32 |
| (CH₃)₂C≡CBr | UV | *n*-C₃H₇CH=CHBr (74–52) | 35 |
| *n*-C₄H₉C≡CH | Peroxide | *n*-C₄H₉CH=CHBr (traces–37) | |
| | | *trans*-C₄H₉CH—CBrCO₂H₃ (95) | 33 |
| C₂H₃C≡CCO₂H | None added | CHBr=CH(CH₂)₃CO₂H | 40 |
| HC≡C(CH₂)₃CO₂H | Perbenzoic acid | | |

*Note.* References 385 to 631 are on pp. 371–376.

† Equal amounts of the two isomers were obtained

‡ The product was isolated as the ω-hydroxy acid

§ The formation of this product was inhibited by catechol; hence a radical path was assumed

TABLE IX—*Continued*

C. *Addition of Hydrogen Chloride to Olefins*

| Olefin | Catalyst | Product (Yield, %) | Refs. |
|---|---|---|---|
| $CH_2=CH_2$ | Peroxide | $H(CH_2CH_2)_nCl$ | 49, 425 |
| | | $n$ (%) $\quad$ $n$ (%) | |
| | | 2 (6) $\quad$ 7 (5) | |
| | | 3 (6) $\quad$ 8 (6) | |
| | | 4 (9) $\quad$ 9 (6) | |
| | | 5 (9) $\quad$ 10 (5) | |
| | | 6 (8) $\quad$ >10 (40) | |
| $CH_2ClCH=CH_2$ | Peroxide | $CH_2ClCHClCH_3$ (22) | 48 |
| | | $CH_2ClCH_2CH_2Cl$ (9) | |
| | | 2:1 adduct | |
| $CH_3CH=CH_2$ | Peroxide | $CH_3CHClCH_3$ (27) | 48 |
| | | $CH_3CH_2CH_2Cl$ (4) | |
| $(CH_3)_3CCH=CH_2$ | Peroxide | $(CH_3)_2CHCCl(CH_3)_2$ (5) | 47 |
| | | $(CH_3)_3CCHClCH_3$ (71) | |
| | | $(CH_3)_3CCH_2CH_2Cl$ (24) | |

*Note:* References 385 to 631 are on pp. 371–376.

TABLE X

FORMATION OF CARBON-SULFUR BONDS

A. Addition of Aliphatic Thiols to Olefins

| Thiol | Olefin | Catalyst | Product (%) | Refs |
|---|---|---|---|---|
| CH₃SH | CF₂=CFCl | UV | CARBON... CF₂ClCF₂H (94) | 6 |
| | CHF=CF₂ | X-ray | CH₃SCHFCHF₂ (45) | 6 |
| | | | CH₃SCF₂CH₂F (15) | |
| | CH₂=CHCl | UV + O₃ | CH₃SCH₂CH₂Cl (19–93) | 120, 426 |
| | CH₃=CCl₂ + CO (200–3000 atm) | Peroxide | CH₃S(CH₂)₂CH₂CHO (18) | 81, 427 |
| | CF₂C=CF₂ | X-ray | CH₃SCF₂... (30) | 30 |
| | CH₂=CHCHO | Peroxide | CH₃S(CH₂)₂CHO (86) | 428, 429, 183, 430–432 |
| | CH₂=CH₂ | UV, O₃ + HgSCH₃ | CH₃S(CH₂)₄CO₂H (—) | 183 |
| | CH₂=CH₂ | UV, O₃ + (CH₃)₂Hg + mercuric salt | CH₃S(CH₂)₂OH (93–95) | 433, 434, 429 |
| | | None added | | 183 |
| | CH₃CH₂CH | | | 435 |

| Thiol | | | | |
|---|---|---|---|---|
| C₂H₅SH | CH₂=CHCHO | Peroxide | CH₃SCH(CH₃)CH₂CHO (67) | |
| | CH₃CO₂CH₂=CH₂ | UV + O₃ | CH₂(CH₃)CH₂SCH₃ (93–95) | 113 |
| | CH₃CO₂CH₂ | Peroxide | CH₃CH₂CH₂SC₂H₅ (60) | 120, 426 |
| | CH₃=CCl₂CH₂CO₂H | | | 113 |
| | | UV + acetone | SC₂H₅ (60) | 182 |

TABLE X—Continued

A. Addition of Aliphatic Thiols to Olefins—Continued

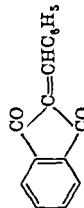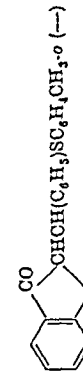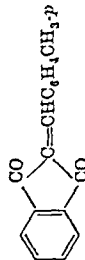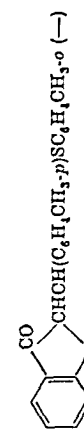| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| CH₃SH (contd.) | (pyridyl)CH=CH₂ | UV, peroxide + diphenyl disulfide | (pyridyl)(CH₂)₂SCH₃ (70) | 109 |
| | C₆H₅CH=CH₂ | UV, O₂ + a mercuric salt | C₆H₅(CH₂)₂SCH₃ (—) | 183 |
| CF₃SH | C₆H₅COCH=CHCO₂H[a] | None | C₆H₅COCH₂CH(SCH₃)CO₂H (—) | 122 |
| | 3,4-CH₂O₂C₆H₃CH₂CH=CH₂ | Peroxide | 3,4-CH₂O₂C₆H₃(CH₂)₃SCH₃ (—) | 436 |
| | 3,4-CH₂O₂C₆H₃CH=CHCH₃ | Peroxide | 3,4-CH₂O₂C₆H₃CH(CH₃)SCH₃ (—) | 436 |
| | CF₂=CFCl | UV | CF₃SCF₂CHFCl (62) <br> CF₃S(CF₂CFCl)₂H (20) <br> CF₃S(CF₂CFCl)₃H (3) | 6 |
| | CF₂=CF₂ | X-ray | CF₃S(CF₂)₂H (53) <br> CF₃S(CF₂)₄H (17) <br> CF₃S(CF₂)₆H (4) | 6 |
| | CHF=CF₂ | UV | CF₃SCHFCHF₂ (83) <br> CF₃SCF₂CH₂F (trace) <br> CF₃S(CHFCF₂)₂H (3.5) | 6 |
| | CH₂=CF₂ | X-ray | CF₃SCH₂CHF₂ (72) | 6 |
| | CF₃CF=CF₂ | UV or x-ray | CF₃SCF₂CHFCF₃ (25) <br> CF₃SCF(CF₃)CHF₂ (31) <br> CF₃S[CF(CF₃)CF₂]₂SCF₃ (13) | 6 |
| | CF₂=CFOCH₃ | UV | CF₃SCF₂CHFOCH₃ (71) | 6 |
| C₂H₅SH | CF₂=CF₂ | Peroxide | 1:1 adduct + higher telomers[b] | 87 |
| | CH₂=CH₂ + CO (2900–3000 atm.) | Peroxide | C₂H₅S(CH₂)₂CHO (11) <br> C₂H₅S(CH₂)₂CH(SC₂H₅)₂ (11) <br> (C₂H₅S)₂S (43) | 427, 81 |
| | CH₂=CHCH₃ | None added | C₂H₅SC₃H₇-n (64) | 88, 177, 437, 438 |
| | CH₂=CHCH₃ + CO (2900–3000 atm.) | Peroxide | C₂H₅SCH₂CH(CH₃)CHO (16) <br> C₂H₅SC₃H₇-n (50) | 427, 81 |
| | CH₂=CHCH=CH₂ | Peroxide + FeCl₂ | 1:1 adduct[b] <br> 2:1 thiol:olefin adduct[c] | 177, 437 |

| | | Catalyst | Product (adduct) | Ref. |
|---|---|---|---|---|
|  CH₃–C structure with CH₃, CH₃ | C₆H₅SCH₂CH₂ structure with CH₃, CH₃ | None added + UV | C₆H₅SCH₂CH₂CO₂CH₃ (23) | 435 |
| | | Peroxide + UV | C₄H₉SCH₂CO₂CH₃ (37) | 69 |
| CH₂=CHCOC₆H₁₁, n | | None added | C₄H₉SCH(CH₃)CH₂Cl (94) | 88 |
| CH₂=CHCO₂C₄H₉ | | None added | C₄H₉SCH₂CH₂Cl (93) | 439 |
| CH₂=CHCN | | None added | C₄H₉SCH₂CH₂SiCl₃ | 179 |
| CH₂=CH(CH₃)₂SiCl₃ | | O₂ | C₄H₉S(CH₂)₃OH (16)ᵈ | 440 |
| CH₂=CH(CH₃)₂OH | | None added | C₄H₉SCH₂CH₂CH₂OH (0) | 88 |
| CH₂=CH(CH₃)₂SiCl₃ | | None added | C₄H₉SCH₂CH(CH₃)SiCl₃ (100) | 88 |
| CH₂=CH(CH₃)₂SiC₄H₉ | | None added | C₄H₉SCH₂CH(CH₃)SiC₄H₉ (80) | 441 |
| | | | | |
| |  C₆H₅SC₆H₁₁ (40) | Peroxide | C₆H₅SC₆H₁₁ (40) | 67 |
| | | | | |
| CH₂=CHOC₄H₉, n | | None added | C₄H₅SCH₂C₄O₄CH₃ (97) | 439 |
| CH₂=CHOCH=CH₂ | | Ascaridole | C₄H₉OCH(SC₄H₉)CH₂SC₄H₉ (5) | 442 |
| CH₂=CHOC₄H₉ | | None added | C₄H₉OCH(SC₄H₉)CH₂SiCl₃ (70) | 108 |
| CH₂=CHOC₄H₉ | | None added | C₄H₉OCH(OC₄H₉)CH₂SC₄H₉ (90) | 108 |
| CH₂=CHOC₄H₉ | | Peroxide | C₄H₉OCH(SC₄H₉)CH₂SiC₄H₉ (103) | 443 |
| CH₂=CHOC₄H₉ | | None added | C₄H₉OCH₂CH₂SiC₄H₉ (173–83) | 444 |
| CH₂=CHC₂H₅ | | Ascaridole + UV | C₆H₅S(CH₂)₃S(CH₃)C₆H₅ (61) | 445 |
| CH₂=CHCl=CH₂ | | Peroxide | CH₂(OSSC₄H₉)CH(CH₃)CH(OCOCH₃) (31) | 174 |
| CH₂=CHCl=CH₂ | | Peroxide | C₆H₅SCH₂CH₂OC₄H₉ (29) | 445 |
| CH₂=CHOC₄H₉, n | | | C₄H₉S₂C₄H₉, n | 67 |

Note: Reference 283 to 631 are on pp. 371–376.
ᵃ The acid was (resolved in aqueous sodium bicarbonate.
ᵇ The structures were not determined.
ᶜ No yield or structure was given for this adduct.
ᵈ The product contained 13–14% of the normal adduct, C₂H₅SCH(CH₃)S(CH₃)CH₂OH.
ᵉ The product contained 1% of the normal adduct, C₂H₅SCH(CH₃)OC₄H₉OH.

TABLE X—Continued

A. Addition of Aliphatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_2H_5SH$ (contd.) | [benzothiazol-2-yl]–$SCH=CH_2$ | Azonitrile | [benzothiazol-2-yl]–$SCH_2CH_2SC_2H_5$ (—) | 446 |
| | $CH_2=CHSC_6H_4CH_3\text{-}p$ | None added | $C_2H_5S(CH_2)_2SC_6H_4CH_3\text{-}p$ (—) | 447 |
| | $CH_3CH=CHSC_6H_5$ | Azonitrile | $C_2H_5SCH(CH_3)CH_2SC_6H_5$ (82) | 448 |
| | $CH_2=C(CH_3)SC_2H_5$ | Azonitrile | $C_2H_5SCH_2CH(CH_3)SC_2H_5$ (81) | 448 |
| | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxido | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SC_2H_5$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxido | $3,4\text{-}CH_2O_2C_6H_3CH(CH_3)SC_2H_5$ (—) | 436 |
| | $n\text{-}C_6H_{13}CH=C(SC_2H_5)_2$ | Azonitrile | $n\text{-}C_6H_{13}CH(SC_2H_5)CH(SC_2H_5)_2$ (8) | 444 |
| | $CH_2=CHC_{14}H_{29}\text{-}n$ | UV, or FeCl₂ + peroxido | $C_2H_5SC_{16}H_{33}\text{-}n$ (94–97) | 177, 437, 438, 449, 450 |
| $ClCH_2CH_2SH$ | [cyclohexene] | Peroxido + CrCl₃ | [cyclohexyl]–$SCH_2CH_2Cl$ (—) | 177, 437, 438 |
| $CF_3CH_2SH$ | $CF_3CF=CF_2$ | UV | $CF_3CH_2SCF_2CHFCF_3$ (46); $CF_3CH_2SCF(CF_3)CHF_2$ (20) | 0 |
| $HOCH_2CH_2SH$ | $CH_2=CHCl$ | (n-C₅H₁₁)₂S₂ + UV | $HOCH_2CH_2SCH_2CH_2Cl$ (100) | 185, 451 |
| | $CH_2=CHCN$ | None added | $HOCH_2CH_2SCH_2CH_2CN$ (91) | 452 |
| | $CH_2=CHCH_2OH$ | None added | $HOCH_2CH_2S(CH_2)_3OH$ (50) | 453, 454 |
| | $CH_3CO_2CH=CH_2$ | None added | $CH_3CO_2CH_2CH_2SCH_2CH_2OH$ (51) | 455 |
| | [cyclohexene] | None added | [cyclohexyl]–$SCH_2CH_2OH$ (—) | 453 |
| | $CH_2=CHSCH_2$ | None added | $HO(CH_2)_2S(CH_2)_2SCH_2$; $HO(CH_2)_2S(CH_2)_2OCH_2$ (—) | 440 |
| | $CH_2=CHOCH_2$ | | | |
| | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxido | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SCH_2CH_2OH$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxido | $3,4\text{-}CH_2O_2C_6H_3CH(CH_3)SCH_2CH_2OH$ (—) | 436 |
| | $CH_2=CH(CH_2)_8CO_2H$ | None added | $HO(CH_2)_2S(CH_2)_{10}CO_2H$ (—) | 456 |

| | | | |
|---|---|---|---|
| ᵃC₄H₇SH | CH₂=CHCl₃ | UV or UV + (C₂H₅)₃Pb + i-Butyl hydroperoxide Fe(NH₄SO₄)₂ | (n-C₄H₇)₂S (96) | 437, 438 |
| | CH₂=CHCH₃ | | n-C₄H₇SCH₂CH₂CH₃' (63) | 459 |
| | | | C₄H₇SCH₂CH=CHCH₃' ⁿ (10) | |
| | | | n-C₄H₇SₙC₄H₇ (15) | |
| | CH₃COCH=CH₂ | None added | CH₃COCH₂CH₂SC₄H₇-n (0) | 460 |
| | CH₂=CHCOCH₃ | UV + peroxide | n-C₄H₇SCH₂CH₂COCH₃ ⁿ (88) | 69 |
| | | | CH₃COCH(SC₄H₇)CH₂CO₂CH₃ (37) | |
| | | None added | n-C₄H₇SCH(CH₃)CH₂SO₂H)SC₄H₇-n (12) | 441 |
| | CH₂=CHCHCl₂ | UV | n-C₄H₇SCH₂CHCl₂SO₂H₄ (90) | 456 |
| | CH₂=CHCHClCH₃ | | n-C₄H₇SCH₂CHClCH₃)SO₂H (—) | 177, 437, 638 |
| | CH₂=CHClCH₂SO₂H | FeC₄ | (CH₃)₃CSCH₂CHClₙSC₄H₉-n (33) | 145 |
| | CH₂=CClCH=CH₂ | | | 76, 110 |
| (CH₃)₃CSH | | | | |
| ᵇC₄H₇SH | CH₃=C(CH₃)₂ | K₂S₂O₅ UV | n-C₄H₇SCH₂CH₂CClCH₂ + polymer | 88 |
| | | | CH(CH₃)₂SC₄H₇ₙ n-(C₄H₇)SₙC₄H₇-n (0 6) | |
| | CH₃=CHCl | None added | n-C₄H₇SCH₂CH₂C₄H₇ₙ (91) | 442 |
| | CH₃=CHCl₂ | None added | n-C₄H₇SCH₂CHₙClC₄H₇ (93) | 72, 73 |
| | CH₃=CHCH₂OC₄H₇ₙ | X ray | n-C₄H₇SCH(SC₄H₇)CH₂OC₄H₇ₙ (66) | 441 |
| | CH₂=CHOC₄H₇ₙ | Acetonitrile | n-C₄H₇SCH(CH₃)CH₂OCₙH₇ (88) | 442 |
| | CH₂=CH(CH₂)₄CH₃ | None added | CH₃(CH₂)₅CHₙSC₄H₇-n (16) | |
| | | | | |
| | [pyridine structure] N�socCH=CH₂ | Peroxide | [pyridine structure] N⎯SCH(CH₃)CH₂SC₄H₇ₙ (72) | 438 |
| | | | | |
| | CH₂=CH(CH₂)₄SC₄H₇ₙ | Acetonitrile | [naphthalene structure] SC₄H₇ₙ (94)ᵈ | 441 |
| | [naphthalene structure] | None added | | 481 |

Note References 245 to 431 are on pp. 271-276.
ᵇ No structure was given for this product.
ᵈ The product contained 4-5% of the normal adduct, n-C₄H₇SCH(CH₃)OC₄H₇, n

## TABLE X—Continued

### A. Addition of Aliphatic Thiols to Olefins—Continued

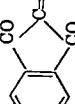| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $n$-C$_4$H$_9$SH (contd.) | 3,4-CH$_2$O$_2$C$_6$H$_3$CH$_2$CH=CH$_2$ | Peroxide | 3,4-CH$_2$O$_2$C$_6$H$_3$(CH$_2$)$_3$SC$_4$H$_9$-$n$ (—) | 436 |
| | 3,4-CH$_2$O$_2$C$_6$H$_3$CH=CHCH$_3$ | Peroxide | 3,4-CH$_2$O$_2$C$_6$H$_3$CH$_2$CH(CH$_3$)SC$_4$H$_9$-$n$ (—) | 436 |
| | CH$_2$=C(CO$_2$CH$_3$)(CH$_2$)$_2$-CH(CO$_2$CH$_3$)CO$_2$CH$_3$ | UV + binoctyl | $n$-C$_4$H$_9$SCH$_2$-CH(CO$_2$CH$_3$)(CH$_2$)$_2$CH(CH$_3$)CO$_2$CH$_3$ (—); $n$-C$_4$H$_9$SCH$_2$-C(CO$_2$CH$_3$)(CH$_2$)$_2$CH(CH$_3$)CO$_2$CH$_3$ (—); CH$_2$CH(CO$_2$CH$_3$)(CH$_2$)$_2$CH(CH$_3$)CO$_2$CH$_3$ | 206 |
| | CH$_2$=CH(CH$_2$)$_8$CO$_2$H | UV | $n$-C$_4$H$_9$S(CH$_2$)$_{10}$CO$_2$H (—) | 456 |
| | ![cyclohexane with OCH=CH$_2$ and CH(CH$_3$)$_2$ groups] | None added | OCH$_2$CH$_2$SC$_4$H$_9$-$n$ (—) CH(CH$_3$)$_2$ | 462 |
| (CH$_3$)$_2$CHCH$_2$SH | CH$_2$=CHCH(CH$_3$)(C$_6$H$_5$)$_2$ | Peroxide | $n$-C$_4$H$_9$S(CH$_2$)$_2$C(CH$_3$)(C$_6$H$_5$)$_2$ (25) | 463 |
| C$_2$H$_5$CH(CH$_3$)SH | CH$_2$=C(CH$_3$)CHOHCH$_3$ | Peroxide | (CH$_3$)$_2$CHCH$_2$SCH$_2$CH(CH$_3$)CHOHCH$_3$ (—) | 464 |
| (CH$_3$)$_3$CSH | CH$_3$CO$_2$CH=CH$_2$ | UV | CH$_3$CO$_2$(CH$_2$)$_2$SCH(CH$_3$)C$_2$H$_5$ (—) | 110 |
| | CH$_2$=CHClCH=CH$_2$ | $t$-Butyl hydroperoxide + Fe(NH$_4$SO$_4$)$_2$ | $t$-C$_4$H$_9$SCH$_2$CH$_2$OC$_4$H$_9$-$t'$ (9); ($t$-C$_4$H$_9$OC$_4$H$_9$)$_2'$ (25) | 459 |
| | CH$_3$CO$_2$CH=CH$_2$ | UV | CH$_3$CO$_2$(CH$_2$)$_2$SC(CH$_3$)$_3$ (—) | 110 |
| | ![pyridine ring with CH=CH$_2$] | UV | ![pyridine ring with (CH$_2$)$_2$SC(CH$_3$)$_3$] (—) | 109 |
| C$_2$H$_5$OCH$_2$CH$_2$SH | 3,4-CH$_2$O$_2$C$_6$H$_3$CH$_2$CH=CH$_2$ | Peroxide | 3,4-CH$_2$O$_2$C$_6$H$_3$(CH$_2$)$_3$SCH$_2$CH$_2$OC$_2$H$_5$ (—) | 436 |
| | 3,4-CH$_2$O$_2$C$_6$H$_3$CH=CHCH$_3$ | Peroxide | 3,4-CH$_2$O$_2$C$_6$H$_3$CH$_2$CH(CH$_3$)SCH$_2$CH$_2$OC$_2$H$_5$ (—) | 436 |
| ![furfuryl/furan CH$_2$SH] | 3,4-CH$_2$O$_2$C$_6$H$_3$CH=CHCH$_3$ | Peroxide | 3,4-CH$_2$O$_2$C$_6$H$_3$CH$_2$CH(CH$_3$)SCH$_2$-![furan] (—) | 436 |

| | | | | | |
|---|---|---|---|---|---|
| n C₉H₁₉SH |  | 3,4 CH₂O₂C₆H₃CH₂CH₂CH=CH₂, 3,4 CH₂O₂C₆H₃CH=CHCH₃ | Peroxide Peroxide | 3,4-CH₃O₂C₆H₃(CH₂)₂SO₂C₉H₁₉-n, 3,4-CH₃O₂C₆H₃CH(CH₃)SO₂C₉H₁₉-n (—) | 436 439 |
| i C₉H₁₉SH* | | | None added | C₉H₁₉SO₂C₆H₁₁ (76) | 465 |
| |  | | UV | SC₆H₁₁-n (84) | 168 |
| C₅H₅COCH(CH₃)SH |  | (CH₃)₂C=CH(CH₂)₂C(CH₃)=CHCH₃ Squalene | None added | 1:1 Adduct (—) | 168 |
| | | | Peroxide + UV | 1:1 Adduct (26), 2:1 Adduct (48) | 168 |
| | | CH₂=CHCH₂Br | | Viscous oil | 168 176 |
| | | CH₂=CHCH₂Cl | Peroxide | C₅H₅COCH(CH₃)S(CH₂)₂CH₂Cl (22) | 176 |
| |  | CH₂=CHCH₂Cl CH₂=CHCH₂OH | Peroxide Peroxide | C₅H₅COCH(CH₃)S(CH₂)₂Cl (20), C₅H₅COCH(CH₃)S(CH₂)₂OH (81) | 176 175 |

Note: References 385 to 631 are on pp 371–376

ᵃ No structure was given for these products
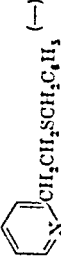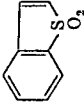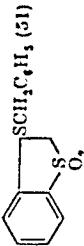
* This thiol, so called "iso-pentanethiol" in ref 168, but no structure is given

## TABLE X—Continued

### A. Addition of Aliphatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_2H_5COCH(CH_3)SH$ (cont.) | $CH_2=CHCH_2NH_2$ | Peroxide | [structure] $N{=}$ ring, $C_2H_5$, $CH_3$, $S$ (43) | 176 |
| | $CH_3CH=C(CH_3)_2$ | Azonitrile | $C_{16}H_{30}N_2S_2{}'$ (23)<br>$C_2H_5COCH(CH_3)SCH(CH_3)CH(CH_3)_2$ (38) | 466 |
| | [cyclohexene, Cl] | Peroxide or UV | [structure] $C_2H_5$, $CH_3$, $S$, $O$ (—) | 176 |
| | [cyclohexene] | Peroxide | $SCH(CH_3)COC_2H_5$ (44) | 466 |
| | [methylcyclohexene, $CH_3$] | Peroxide | $CH_3$ [structure] $SCH(CH_3)COC_2H_5$ (33) | 466 |
| | $C_6H_5CH=CH_2$ | Peroxide | $C_2H_5COCH(CH_3)S(CH_2)_2C_6H_5$ (55) | 466 |
| | $C_6H_5CH=CHCH_2OH$ | Peroxide | $C_6H_5$ [structure] $S(CH_3)COC_2H_5$ (16) | 176 |
| $n\text{-}C_6H_{13}SH$ | $n\text{-}C_6H_{13}CH=CH_2 + CO$<br>(2900–3000 atm.) | Peroxide | $n\text{-}C_6H_{13}SCH_2CH(CHO)C_4H_9\text{-}n$ (8) | 81, 427 |
| | $CH_2=CHB(OC_4H_9)_2$ | UV | $(n\text{-}C_6H_{13})_2S$ (37)<br>$n\text{-}C_6H_{13}S(CH_2)_2B(OC_4H_9)_2$ (93) | 467 |
| | $CH_2=CH(CH_2)_8CO_2H$ | UV | $n\text{-}C_6H_{13}S(CH_2)_{10}CO_2H$ (—) | 456 |
| | [benzothiophene $SO_2$ structure] | Peroxide | [structure] $SC_6H_{13}\text{-}n$, $SO_2$ (34) | 141 |
| | $3,4\text{-}CH_3O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_3O_2C_6H_3(CH_2)_3SC_6H_{13}\text{-}n$ (—) | 436 |
| | $3,4\text{-}CH_3O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_3O_2C_6H_3CH_2CH(CH_3)SC_6H_{13}\text{-}n$ (—) | 436 |

| | | | | |
|---|---|---|---|---|
| $c$-C₆H₁₁SH | CH₂=ClCH₂OH | Peroxide | (SCH₃)₃CH (—) | 464 |
| | (cyclohexene) | UV | (84) | 468 |
| | 3,4 CH₂O₂C₆H₃CH₂CH=CHCl₂ | Peroxide | 3,4 CH₂O₂C₆H₃CH₂S | 435 |
| | 3,4 CH₂O₂C₆H₃CH=CHCl₂ | Peroxide | 3,4 CH₂O₂C₆H₃CH₂S (—) | 436 |
| *n*-C₇H₁₅CH(CH₂)₈H | CH₂=ClCHCl·CH₃ | None added | n C₆H₁₃OCH₂SCH₂C₆H₄OC₂H₅, n (—) | 439 |
| | n C₆H₁₃SCH₂CH=CH₂ | None added | n C₆H₁₃OCH₂CH₂SCH₂C₆H₄OC₂H₅, n (86) | 443 |
| | 3,4 CH₂O₂C₆H₃CH=CHCl₂ | None added | 3,4 CH₂O₂C₆H₃SCH₂C₆H₄OC₂H₅, n (86) | 409 |
| | 3,4 CH₂O₂C₆H₃CH₂CH=CHCl₂ | Peroxide | 3,4 CH₂O₂C₆H₃CH₂CH₂CH₂SCH₂C₆H₄OC₂H₅ | 436 |
| | 3,4 CH₂O₂C₆H₃CH=CHCl₂ | Peroxide | 3,4 CH₂O₂C₆H₃CH₂CH₂CHCl₂SCH₂C₆H₄OC₂H₅, *p* | 436 |
| 11OC₈H₁₇CHOH₂CH₂SH | (cyclopentanone structure) | Acetonitrile | 1:1 Adduct (—) | 181 |
| *c*-C₆H₁₁C₆H₅SH | 3,4 CH₂O₂C₆H₃CH₂CH=CHCl₂ | Peroxide | 2,4 CH₃O₂C₆H₃SCH₂C₆H₅C₆H₅Cl *o* (—) | 436 |
| *p* C₆H₁₁ C₆H₅SH | 3,4 CH₂O₂C₆H₃CH₂CH=CHCl₂ | Peroxide | 3,4 CH₃O₂C₆H₃CH₂SCH₂C₆H₅C₆H₅Cl *p* (—) | 436 |
| | 3,4 CH₂O₂C₆H₃CH=CHCl₂ | Peroxide | 3,4 CH₂O₂C₆H₃CH₂CH₂SO₂C₆H₅ | 436 |
| C₆H₅C₆H₅SH | CH₂=CH·CH₂Cl | UV | ClOCH₂CHOCl₂SO₂C₆H₅ (—) | 121 |
| | CH₂=CHClClO | None added | CH₂ClCHClSC₆H₅ (—) | 135 |
| | CH₂=CHCHOH | Peroxide | C₇H₁₅CHOHCH₂SC₆H₅, n (172) | 113 |
| | CH₂=CHCHO | Peroxide | C₇H₁₅CH₂SCH₂CHO (51) | 113, 135 |
| | CH₂=CHCH=CH₂ | Peroxide | C₆H₅C₆H₅CH₂SC₆H₅ (70) | 110 |

Note: References 355 to 431 are on pp. 371–376.
*ᵖ* No structure was given for this product.

## TABLE X—Continued

### A. Addition of Aliphatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5CH_2SH$ (contd.) | $CH_3CH=CHCO_2H$ | Peroxide | $C_6H_5CH_2SCH(CH_3)CH_2CO_2H$ (95) | 113, 131 |
| | $CH_2=C(CO_2H)CH_2CO_2H$ | Azonitrile | $C_6H_5CH_2SCH_2CH(CO_2H)CH_2CO_2H$ (40) | 470 |
| | $CH_3CH=C(OH)_2$ | None added | $C_6H_5CH_2SCH(CH_3)CH(CH_3)_2$ᴺ (—) | 63 |
| |  | Sunlight or peroxide |  $SCH_2C_6H_5$ (97) | 113, 166, 168, 471 |
| | $CH_3CO_2CH_2C(CH_3)=CH_2$ | Peroxide | $CH_3CO_2CH_2CH(CH_3)CH_2SCH_2C_6H_5$ (73) | 113 |
| | $CH_2=CHSi(CH_3)_2OC_2H_5$ | None added | $C_6H_5CH_2S(CH_2)_2Si(CH_3)_2OC_2H_5$ (26) | 472 |
| |  $N\text{-}CH=CH_2$ | Peroxide |  $CH_2CH_2SCH_2C_6H_5$ (—) | 436, 109 |
| | $CH_2=CHSi(CH_3)(OC_2H_5)_2$ | None added | $C_6H_5CH_2S(CH_2)_2Si(CH_3)(OC_2H_5)_2$ (—) | 472 |
| |  | Peroxide |  $SCH_2C_6H_5$ (51) | 141 |
| | $C_6H_5CH=CH_2$ | Peroxide | $C_6H_5CH_2S(CH_2)_2C_6H_5$ (93) | 113, 460 |
| | $CH_2=CHSi(OC_2H_5)_3$ | None added | $C_6H_5CH_2S(CH_2)_2Si(OC_2H_5)_3$ (34) | 436 |
| | $C_6H_5CH=CHCO_2H$ | Peroxide | $C_6H_5CH_2SCH(C_6H_5)CH_2CO_2H$ (35) | 472 |
| | $C_6H_5C(CH_3)=CH_2$ | None added | $C_6H_5CH_2SCH_2CH(CH_3)C_6H_5$ (—) | 113 |
| | $C_6H_5CH=CHCH_2OH$ | Peroxide | $C_6H_5CH_2SCH(C_6H_5)CH_2OH$ (17) | 63 |
| | | | | 113 |

| | | | | |
|---|---|---|---|---|
| $C_6H_5$ $CH_3$ | | | $CH_2SCH_2C_6H_5$ | 63 |
|  None added | | |  $C_6H_5COCH(CH(CO_2H))SCH_2C_6H_5$ (—) | |

| | | | |
|---|---|---|---|
| $C_6H_5COCH=CHCO_2H$ | None added | $C_6H_5SCH(C_6H_4)CH_2CH_2CO_2C_6H_5^g$ (—) | 122 |
| $C_6H_5CH=CHCO_2H$ | None added | $3,4\text{-}CH_3O_2C_6H_4\text{-}SCH_2C_6H_5$ | 123 |
| $3,4\text{-}CH_3O_2C_6H_3CH_2$—CHCH $=$ CH$_2$ | Peroxide | $3,4\text{-}CH_3O_2C_6H_3CH_2\text{-}SCH_2C_6H_{11}$ | 436 |
| $3,4\text{-}CH_3O_2C_6H_3CH_2$—CH $=$ CHCH$_3$ | Peroxide | $3,4\text{-}CH_3O_2C_6H_3CH_2\text{-}CHCH_2$—CHCH$_3$ | 436 |
| $CH_3CO_2C_6H_4CH_2CH$—CH $=$ CH$_2$ | Peroxide | $CH_3CO_2C_6H_4CH_2CH_2\text{-}CH_2SCH_2C_6H_{11}$ | 113 |
| $C_6H_5CH=CH(CH_2)_5CO_2H$ | UV | $C_6H_5CH(SCH_2)_6CO_2H^j$ (38) | 456 |
| $C_6H_5CH=CH(CH_2)_5CO_2H^i$ | None added | $C_6H_5CH(SCH_2C_6H_5)CH_2CO_2H^i$ (—) | 123 |

| | | | |
|---|---|---|---|
|  $C$—CH$=$CHCH$_2$C$_6H_5$ | None added |  CHCH(C$_6H_5$)CH$_2$ $p$)SCH$_2C_6H_5$ (—) | 136 |

| | | | |
|---|---|---|---|
|  $C$—CH$=$CHC$_6H_4NO_2$ $o$ | None added |  CHCH$(C_6H_4NO_2$ $o$)SCH$_2C_6H_5$ (—) | 136 |

*Note:* References 283 to 631 are on pp. 371–376.

f No structure was given for this product.

g The product was isolated as the sulfone.

h The structure was not proved.

i The configuration of the product is not known.

j The product was isolated as the oxime.

### TABLE X—Continued

#### A. Addition of Aliphatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5CH_2SH$ (contd.) | [phthalide/phthalic anhydride structure] $C=CHC_6H_4NO_2\text{-}m$ | None added | [structure] $CHCH(C_6H_4NO_2\text{-}m)SCH_2C_6H_5$ (—) | 130 |
| | [structure] $C=CHC_6H_4NO_2\text{-}p$ | None added | [structure] $CHCH(C_6H_4NO_2\text{-}p)SCH_2C_6H_5$ (—) | 136 |
| | [structure] $C=CHC_6H_5$ | None added | [structure] $CHCH(C_6H_5)SCH_2C_6H_5$ (—) | 136 |
| | [structure] $C=CHC_6H_4CH_3\text{-}p$ | None added | [structure] $CHCH(C_6H_4CH_3\text{-}p)SCH_2C_6H_5$ (—) | 136 |
| $n\text{-}C_7H_{15}SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SC_7H_{15}\text{-}n$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2CH(CH_3)SC_7H_{15}\text{-}n$ (—) | 436 |
| | $CH_2=CH(CH_2)_8CO_2H$ | UV | $n\text{-}C_7H_{15}S(CH_2)_{10}CO_2H$ (62) | 450 |
| $p\text{-}ClC_6H_4OCH_2CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3\text{-}$ $CH(CH_3)SCH_2CH_2OC_6H_4Cl\text{-}p$ (—) | 436 |
| $C_6H_5CH_2CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SCH_2CH_2C_6H_5$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2CH(CH_3)SCH_2CH_2C_6H_5$ (—) | 436 |
| $C_6H_5OCH_2CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SCH_2CH_2OC_6H_5$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2CH(CH_3)SCH_2CH_2OC_6H_5$ (—) | 436 |

| | | | |
|---|---|---|---|
| (O)CH₂OCH(CH₃)₂SH | 3,4 Cl₂C₆H₃CH₂CH₂CH=CH₂ | Peroxide | 3,4 CH₃OC₆H₃CH₂CH₂SₙC₄H₉, π-(−) | 436 |
| | 3,4 Cl₂C₆H₃CH₂CH=CHCH₃ | Peroxide | 3,4 CH₃O₂C₆H₃CH₂CH₂CH(CH₃)SₙC₄H₉, π-(51) | 436 |
| | 4 ClC₆H₄CH₂CH₂CH=CHCH₃ | Peroxide or UV | 4 ClC₆H₄CH₂CH₂CH₂CH(CH₃)SₙC₄H₉-n, π-(−) | 435 |
| | 3 CH₃O 4 HOC₆H₃CH₂CH=CH₂ | Peroxide | 3 CH₃O 4 HOC₆H₃CH₂CH₂SₙC₄H₉-n, π-(−) | 436 |
| n-C₄H₉SH | CH₂=CHCH₂OC₆H₄f | UV | n-C₄H₉SCH₂CH(CH₃)CH₂OC₆H₄f | 429, 473 |
| | 3,4 Cl₂C₆H₃CH₂CH₂CH=CH₂ | Peroxide | 3,4 CH₃OC₆H₃CH₂CH₂CH₂SCH(CH₃)₂C₄H₉, π-(−) | 436 |
| n-C₄H₉SH + (O)C₄H₉SH | 3,4 Cl₂C₆H₃CH₂CH=CH₂ | Peroxide | 3,4 CH₃OC₆H₃CH₂CH₂CH₂SₙC₄H₉-n, f (−) | 436 |
| | 2,4 Cl₂C₆H₃OCH₂CH=CH₂ | Peroxide | 3,4 CH₃OC₆H₃N(CH₃)₃SSC₄H₉-n, π-(−) | 436 |
| | 3,4 Cl₂C₆H₃OCH₂CH=CH₂ | Peroxide | 3,4 CH₃OC₆H₃OCH₂CH₂OC₄H₉, π-(−) | 436 |
| | (norbornene) | Peroxide | | 436 |
| n-C₄H₉OCH₂CH₂OC(CH₃)₂SH | (norbornene) | None added | n-C₄H₉OCH₂CH₂OC₁₀H₁₇SC₁₀H₁₇ (79) | 465 |

*Note:* References 385 to 631 are on pp. 371–376.

f No structure was given for this product.

TABLE X—Continued

A. Addition of Aliphatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5CH_2CH(CH_3)SH$ | $C_6H_5CH=CHNO_2$ | Peroxide | $C_6H_5CH_2CH(CH_3)SCH(C_6H_5)CH_2NO_2$ (44) | 124 |
| | $p\text{-}O_2NC_6H_4COCH=CHC_6H_5$ | Peroxide | $C_6H_5CH_2CH(CH_3)SCH(C_6H_5)CH_2\text{-}$ $COC_6H_4NO_2\text{-}p$ (74) | 124 |
| | $C_6H_5COCH=CHCOC_6H_5$ $(trans)$ | Peroxide | $C_6H_5CH_2CH(CH_3)SCH(COC_6H_5)CH_2COC_6H_5$ (91) | 124 |
| $C_6H_5CH_2OCH_2CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SCH_2CH_2OCH_2C_6H_5$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)SCH_2CH_2OCH_2C_6H_5$ (—) | 436 |
| $p\text{-}CH_3C_6H_4OCH_2CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)SCH_2CH_2OC_6H_4CH_3\text{-}p$ (—) | 436 |
| $\underset{O}{\overset{CH_2O(CH_2)_2\text{-}}{\boxed{\phantom{xx}}}}O(CH_2)_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2)_2O(CH_2)_2OCH_2\boxed{\phantom{x}}O$ (—) | 436 |
| $p\text{-}(i\text{-}C_3H_7)C_6H_4CH_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SCH_2C_6H_4(C_3H_7\text{-}i)\text{-}p$ (—) | 436 |
| $C_6H_5(OCH_2CH_2)_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3S(CH_2CH_2O)_2C_6H_5$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2CH(CH_3)S(CH_2CH_2O)_2C_6H_5$ (—) | 436 |
| $o\text{-}CH_3OC_6H_4O(CH_2)_3SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3S(CH_2)_3OC_6H_4OCH_3\text{-}o$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2)_3OC_6H_4OCH_3\text{-}o$ (—) | 436 |
| $m\text{-}CH_3OC_6H_4O(CH_2)_3SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3S(CH_2)_3OC_6H_4OCH_3\text{-}m$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2)_3OC_6H_4OCH_3\text{-}m$ (—) | 436 |
| $p\text{-}CH_3OC_6H_4O(CH_2)_3SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3S(CH_2)_3OC_6H_4OCH_3\text{-}p$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2)_3OC_6H_4OCH_3\text{-}p$ (—) | 436 |
| $n\text{-}C_{10}H_{21}SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3SC_{10}H_{21}\text{-}n$ (—) | 436 |
| $n\text{-}C_6H_{13}O(CH_2)_2O(CH_2)_2SH$ | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2CH(CH_3)SC_{10}H_{21}\text{-}n$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3\text{-}$ $S(CH_2)_2O(CH_2)_2OC_6H_{13}\text{-}n$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2)_2O(CH_2)_2OC_6H_{13}\text{-}n$ (—) | 436 |
| $n\text{-}C_4H_9(OOCH_2CH_2)SH$ | $3,4\text{-}CH_2O_2C_6H_3CH_2CH=CH_2$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3(CH_2)_3S(CH_2CH_2O)_3C_4H_9\text{-}n$ (—) | 436 |
| | $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH_2\text{-}$ $CH(CH_3)S(CH_2CH_2O)_3C_4H_9\text{-}n$ (—) | 436 |

| | | | |
|---|---|---|---|
| n-C$_4$H$_9$OC$_2$H$_4$-<br>[OC$_2$H$_4$]$_2$C$_4$H$_9$SH | 3,4 CH$_2$ClC$_6$H$_4$CH$_2$CH$_2$CH$_3$ | Peroxide | 3,4 CH$_2$C$_6$H$_4$CH$_2$CH(CH$_3$)-<br>S[OC$_2$H$_4$]$_2$OC$_4$H$_9$-$n$ $m$ (—) | 438 |
| | 3,4 CH$_2$ClC$_6$H$_4$CH=CHCH$_3$ | Peroxide | 3,4 CH$_2$C$_6$H$_4$CH$_2$CH$_2$CH$_2$S(CH$_3$)$_3$, $m$ (—) | 438 |
| n-C$_8$H$_{17}$SH | CH$_2$=CHCH$_2$)$_2$O$_3$H | UV | n-C$_8$H$_{17}$SCH$_2$CH(O)CH$_2$- $n$ | 456 |
| C$_4$H$_9$OC$_2$H$_4$O(OC$_2$H$_4$)$_2$SH | 3,4 CH$_2$ClC$_6$H$_4$CH$_2$CH=CH$_2$ | Peroxide | 3,4 CH$_2$C$_6$H$_4$(CH$_2$)$_3$SC$_2$H$_4$- $n$ | 438 |
| | CH$_2$=CHCH(CH$_3$)$_2$ C$_6$H$_5$ $+ n$ (—) | | 3,4 CH$_2$ClC$_6$H$_4$(CH$_2$)$_3$SC$_2$H$_4$O-<br>(C$_2$H$_4$O)$_2$C$_4$H$_9$ $m$ (—) | 438 |
| C$_{12}$H$_{25}$SH | CP=CPCl | Peroxide + UV | n-C$_{12}$H$_{25}$SCF$_2$CHCl $_2$ (99) | 438 |
| | CH$_2$=ClCOC$_6$H$_4$H$_3$ | Peroxide | n-C$_{12}$H$_{25}$SCH$_2$CH(CO$_2$C$_6$H$_4$H$_5$)SCH$_2$-<br>OC$_2$H$_4$O(C$_2$H$_4$O)$_3$H $n$ (—) | 119 |
| | | Peroxide | n-C$_{12}$H$_{25}$SC$_6$H$_4$SC$_{12}$H$_{25}$-$n$ | 89 |
| | | | $n = 1$ (17) | |
| | | | $n = 2$ (21) | |
| | | | $n = 3$ (46) | |
| | | | $n = 4$ (32) | |
| (CH$_2$=CHCH$_2$)$_2$O | (C$_2$H$_5$)$_3$S | UV | n-C$_{12}$H$_{25}$S(CH$_2$)$_3$OCH$_2$-<br>n-C$_{12}$H$_{25}$S(CH$_2$)$_3$O(CH$_2$)$_3$SC$_{12}$H$_{25}$-$n$ (—) | 474 |



| | | | |
|---|---|---|---|
| | | (C$_6$H$_5$)$_2$S | UV | $_2$N·(CH$_3$)$_2$SC$_{12}$H$_{25}$-$n$    (60) | 109 |
| C$_6$H$_5$CH$_2$—CH$_2$ | | (C$_6$H$_5$)$_2$S + UV | n-C$_{12}$R$_{25}$S(C$_6$H$_4$CH$_2$CH$_2$)$_{4,n}$H (73) | 90 |
| | 3,4 CH$_2$C$_6$H$_4$CH$_2$CH=CH$_2$ | Peroxide | 3,4 CH$_2$C$_6$H$_4$(CH$_2$)$_3$SC$_{18}$H$_{33}$-$n$ $m$ (—) | 438 |
| | 3,4 CH$_2$=CHCH$_2$C$_6$H$_4$H | UV | n-C$_{18}$H$_{37}$S(CH$_2$)$_3$CO$_2$H $n$ | 456 |
| | 3,4 CH$_2$ClC$_6$H$_4$(CH$_2$)$_2$CO$_2$H | Peroxide | 3,4 CH$_2$C$_6$H$_4$(CH$_2$)$_3$CO$_2$H $n$ | 456 |
| C$_{18}$H$_{37}$SH | CH$_2$=CHC$_6$H$_5$ | Peroxide | n-C$_{18}$H$_{37}$SCH$_2$CH$_2$C$_6$H$_5$ $n$ | 67 |
| | CH$_2$=C(CH$_3$)$_2$ $n$ | Peroxide | n-C$_{18}$H$_{37}$SCH$_2$CH$_2$(CH$_3$)$_2$ $n$ | 67 |
| | CH$_2$=CHOC$_2$H$_5$ $n$ | None added | n-C$_{18}$H$_{37}$SCH$_2$CH$_2$CH$_2$CO$_2$C$_2$H$_5$ (80) | 137 |
| | CH$_2$=CHCO$_2$C$_2$H$_5$ $n$ | Peroxide | n-C$_{18}$H$_{37}$SCH$_2$CH$_2$ $n$ | 67 |
| | CH$_2$=CHC$_6$H$_4$H $n$ | Peroxide | n-C$_{18}$H$_{37}$SC$_6$H$_4$H $n$ | 67 |
| | CH$_2$=CHC$_6$H$_4$H $n$ | Peroxide | n-C$_{18}$H$_{37}$SC$_6$H$_4$H $n$ | 67 |

## TABLE X—Continued

### B. Addition of Mercapto Acids to Olefins

| Mercapto Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HSCH₂CO₂H | CH₂=CHCN | Peroxide | NC(CH₂)₂SCH₂CO₂H (74) | 475 |
| | CH₂=CHCO₂H | Peroxide | HO₂C(CH₂)₂SCH₂CO₂H <br> HO₂CCH(CH₃)SCH₂CO₂H } (69) | 475 |
| | CH₂=CHCH₂Cl | Peroxide | C₇H₅ClO₂S′ (74) | 476 |
| | CH₃COCH=CHCO₂H | None added | CH₃COCH₂CH(CO₂H)SCH₂CO₂H (52) | 477 |
| | CH₂=CHCH₂SCH₂CO₂H | Peroxide | HO₂CCH₂S(CH₂)₂SCH₂CO₂H (70) | 478 |
| | (CH₃)₃SiCH=CH₂ | None added | (CH₃)₃Si(CH₂)₂SCH₂CO₂H (25) | 479, 480 |
| | [cyclohexene structure] | None added | [cyclohexane]SCH₂CO₂H (83) | 466, 468, 108, 481 |
| | (CH₃)₃SiCH₂CH=CH₂ | None added | (CH₃)₃Si(CH₂)₃SCH₂CO₂H (54) | 479, 480 |
| | [bicyclic diene structure] | None added | [bicyclic structure]SCH₂CO₂H[l] (-) | 482 |
| | [methyl-cyclohexene structure, CH₃] | Peroxide | [cyclohexane with CH₃ / SCH₂CO₂H] (100) | 466, 108 |
| | C₆H₅CH=CH₂ | None added | C₆H₅(CH₂)₂SCH₂CO₂H (91) | 466 |
| | n-C₆H₁₃CH=CH₂ | None added | n-C₈H₁₇SCH₂CO₂H (95) | 483 |
| | (CH₃)₃SiOSi(CH₃)₂CH₂CH₂CH=CH₂ | None added | (CH₃)₃SiOSi(CH₃)₂(CH₂)₃SCH₂CO₂H (46) | 479, 480 |
| | p-CH₃C₆H₄SO₂CH=CH₂ | None added | p-CH₃C₆H₄SO₂(CH₂)₂SCH₂CO₂H (—) | 447 |
| | n-C₇H₁₅CH=CH₂ | None added | n-C₉H₁₉SCH₂CO₂H (95) | 483 |

| | | | |
|---|---|---|---|
| C₆H₅COCH=CHCO₂H, 3,4 CH₂O₂C₆H₃CH=CH—CH₃, 3,4(CH₃O)₂C₆H₃CH=CHCH₃ | None added[h] Peroxide Peroxide | C₆H₅COCH₂CH(CO₂H)SCH₂CO₂H (—) 3,4 CH₂O₂C₆H₃CH₂CH₂SC₃H₇ (69) 3,4(CH₃O)₂C₆H₃CH₂CH₂SCH₂CO₂H (75) | 122 438 436 |
|  | None added | 1,1 adduct (70) | 463 |
| p-CH₃OC₆H₄CH=CH—CHCH₃ | Peroxide + UV | C₁₄H₁₆O₄S² (90) | 478 |
| CH₃ cyclohexene | UV | C₈H₁₆O₃S (89) | 476 |
| CH₃O—CH=CH₂ (Dipentene) | | | |
| CH₃O—CH=CH₂ (+ limonene) | Peroxide | C₁₄H₂₆O₄S² (64) or C₁₄H₂₆O₄S² (85) | 476 |

Note  References 325 to 631 are on pp. 371–378.
f No structure was given for the product.
g The configuration of this product was not given.
h The reactants were dissolved in aqueous sodium bicarbonate.

TABLE X—*Continued*

B. *Addition of Mercapto Acids to Olefins—Continued*

| Mercapto Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HSCH$_2$CO$_2$H (*contd.*) | | | | |
| | CH$_3$C=CH$_2$ (−-Limonene) | Peroxide | C$_{11}$H$_{21}$O$_4$S$_2$$^f$ (80) | 476 |
| | (α-Pinene) | UV | C$_{12}$H$_{20}$O$_2$S$^f$ (63) | 176 |
| | (β-Pinene) | Peroxide | C$_{12}$H$_{20}$O$_2$S$^f$ (82) | 476 |

| | | | | |
|---|---|---|---|---|
|   (2-Carbomethoxy) | | | | |
| $(CH_3)_2C=CHCH_2)_2C(CH_3)_2C=CHCH_3$ | UV | None added | $(CH_3)_2C=CHCH_2-$ CHCH₂CH(CH₃)₂SCH₂CO₂H (49) (CH₃)₂CHCHCH(CH₃)₂CH₂]₂ CHCH₂CH=C(CH₃)₂N₃C₃H₇]₂CO₂H (−) $C_nH_{2n}O_xS^z$(83) | 478 |
| $n-C_6H_{13}CH=CH_2$ | | None added | $n-C_8H_{17}N_3CH_2CO_2H$ (95) | 108 |
| $CH_2=CHCH(CH_2)_3CO_2H$ | | None added | $HO(CH_2)_5N_3(C_4H_9)CH_2$ (87) | 483 |
| $n-C_6H_{13}CH=CH_2$ | | None added | $n-C_8H_{17}N_3(C_4H_9)CH_2$ (95) | 485, 456 |
| $n-C_4H_9CH(CH_2)_3CH_2CH=CH_2$ | | None added | $n-C_4H_9CHCH(CH_2)_3CH_2CH=C_4H_9N_3C_4H_9$ (95) | 483 |
| $C_8H_{17}CH=CH_2$ | | None added | $C_{10}H_{21}N_3C_4H_9$ (−) | 481 |
| | | None added | $C_nH_{2n}SCH_2CO_2H$ (−) | 485 |
| | | None added | $C_nH_{2n}O_xS^z$ (96) | 486 |
| $n-C_9H_{17}CH=CHCH_2$ CH=CH(CH_2)_7CO_2H (Linoleic acid) | | None added | $CH_3(CH_2)_4CH(SCH_2CO_2H)(CH_2)_{11}CO_2H$ (79) | 180 476, 485 |
| $n-C_5H_{11}CH=CHCH_2CH_2CO_2H$ (Oleic acid) | | Peroxide | $CH_3CH_2)_3CH(SCH_2CO_2H)(CH_2)_{11}CO_2H$ (87) | 485 |
| $n-C_5H_{11}CH_2=CH=CH(CH_2)_7CO_2H$ (Elaidic acid and trans) | | | | |

Note: References 355 to 631 are on pp. 371–376
† No structure was given for the product.

TABLE X—Continued

B. Addition of Mercapto Acids to Olefins—Continued

| Mercapto Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HSCH₂CO₂H (contd.) | n-C₆H₁₃CHOHCH₂-CH=CH(CH₂)₇CO₂H | Air | n-C₆H₁₃CHOH(CH₂)₁₍₉₎·CH(SCH₂CO₂H)(CH₂)₇₍₈₎CO₂H (—) | 180 |
| | n-C₅H₁₁CH=CHCH₂-CH=CH(CH₂)₇CO₂CH₃ (Methyl linoleate) | None added | C₂₁H₃₈O₄S⁷ (two isomers) (40) | 486 |
| | n-C₅H₁₁CH—CH(CH₂)₇CO₂CH₃ n-C₆H₁₃CHOHCH₂- | Peroxide | CH₃(CH₂)₅₍₆₎CH(SCH₂CO₂H)(CH₂)₇₋₍₈₎CO₂CH₃ (—) | 485 |
| | CH=CH(CH₂)₇CO₂CH₃ (Methyl ricinoleate) | Peroxide | n-C₆H₁₃CHOH(CH₂)₁₍₉₎·CH(SCH₂CO₂H)(CH₂)₇CO₂CH₃ (89) | 485 |
| | n-C₅H₁₁CH=CHCH₂-CH=CH(CH₂)₇CO₂C₂H₅ (Ethyl linoleate) | Air | 2:1 Adduct^f (100) | 180 |
| | Ricinoleic acid triglyceride | Air | Triadduct^f (100) | 180 |
| | (CH₃)₃SiCH₂CH=CH₂ | None added | (CH₃)₃Si(CH₂)₃SCH₂CO₂C₂H₅ (63) | 479, 480 |
| | C₆H₅CH=CH₂ | None added | C₆H₅(CH₂)₂SCH₂CO₂C₂H₅ (—) | 114 |
| | (C₂H₅O)₃SiCH₂CH=CH₂ | None added | (C₂H₅O)₃Si(CH₂)₃SCH₂CO₂C₂H₅ (48) | 479, 487 |
| | (C₂H₅)₃Si(CH₂CH—CH₂)₂ | Peroxide | (C₂H₅)₃Si[(CH₂)₃SCH₂CO₂C₂H₅]₂ (86) | 488 |
| | n-C₅H₁₁CH=CHCH₂-CH=CH(CH₂)₇CO₂C₂H₅ (Ethyl linoleate) | Air | 2:1 Adduct^f (100) | 489 |
| | n-C₅H₁₁CH=CH(CH₂)₇CO₂C₄H₉-n | Peroxide | CH₃(CH₂)₄₍₅₎CH(SCH₂CO₂C₂H₅)-(CH₂)₇₋₍₈₎CO₂C₄H₉-n (—) | 485 |
| HSCH₂CH₂CO₂H | (cyclohexene) C₆H₁₀=CH—CH₂ | UV | (cyclohexyl)SCH₂CH₂CO₂H (73) | 468 |
| | C₆H₅CH=CH₂ | None added | C₆H₅(CH₂)₂SCH₂CH₂CO₂H (—) | 490 |
| | (2-methyl-1,4-naphthoquinone) | None added | (2-methyl-3-SCH₂CH₂CO₂H-1,4-naphthoquinone) (30) | 491 |

| | | | | |
|---|---|---|---|---|
| HSCH(CO₂H)CH₂CO₂H | CH₃CHCH=CH₂<br>$\quad$HCCO₂H<br><br>BrCO₂H | Peroxide | ClCH(CO₂H)₂SCH(CO₂H)CH₂CO₂H (35) | 492 |
| | | None added | HO₂CCH₂CHCO₂H)SCH(CO₂H)CH₂CO₂H (43) | 493 |
| | n-C₄H₉CH=CH₂ | Peroxide | /SCH(CO₂H)CH₂CO₂H (75) | 492 |
| | C₆H₅CH₂CH=CH₂ | Peroxide | n-C₆H₁₃SCH(CO₂H)CH₂CO₂H (85) | 492 |
| | (CH₃)₂C=CHCH₃ | Peroxide | C₆H₅CH₂CH₂CH₂SCH(CO₂H)CH₂CO₂H (85) | 492 |
| | | Peroxide | (CH₃)₂CHCH(CH₃)SCH(CO₂H)CH₂CO₂H (75) | 492 |
| | (benzene ring) | Peroxide or UV | /SCH(CO₂H)CH₂CO₂H (83) | 492, 468 |
| | n-C₆H₁₃CH=CH₂ | Peroxide | n-C₆H₁₃SCH(CO₂H)CH₂CO₂H (100) | 492 |
| | (C₆H₅)₂CHCH₂CH=CH₂ | Peroxide | (C₆H₅)₂CHCH₂CH₂CH₂SCH(CO₂H)CH₂CO₂H (92) | 492 |
| | (CH₃)₂C=CH₂ | Peroxide | (CH₃)₃CSCH(CO₂H)CH₂CO₂H (60) | 492 |
| | (cyclohexene, CH₃) | Peroxide | CH₃ /SCH(CO₂H)CH₂CO₂H (73) | 492 |
| | n-C₆H₁₃CH=CH₂ | Peroxide | n-C₈H₁₇SCH(CO₂H)CH₂CO₂H (88) | 492 |
| | (CH₃)₂CHCH₂CH=CH₂ | Peroxide | (CH₃)₂CHCH₂CH₂CH₂SCH(CO₂H)CH₂CO₂H (90) | 492 |
| | (C₂H₅)₂C=CHCH₃ | Peroxide | (C₂H₅)₂CHCH(CH₃)SCH(CO₂H)CH₂CO₂H (45) | 492 |
| | n-C₅H₁₁CH=CH₂ | Peroxide | n-C₇H₁₅SCH(CO₂H)CH₂CO₂H (96) | 492 |
| | n-C₃H₇CH(CH₃)CH=CH₂ | Peroxide | n-C₃H₇CH(CH₃)CH₂CH₂SCH(CO₂H)CH₂CO₂H (94) | 492 |
| | n-C₄H₉CH₂CH=CH₂ | Peroxide | n-C₄H₉CH₂CH₂CH₂SCH(CO₂H)CH₂CO₂H (81) | 492 |
| | n-C₃H₇CH₂CH=CH₂ | Peroxide | n-C₃H₇CH₂CH₂CH₂SCH(CO₂H)CH₂CO₂H (82) | 492 |
| | n-C₅H₁₁CH=CH₂ | Peroxide | n-C₅H₁₁CH₂CH₂SCH(CO₂H)CH₂CO₂H (65) | 492 |
| | n-C₆H₁₃CH=CH₂ | Peroxide | n-C₆H₁₃CH₂CH₂SCH(CO₂H)CH₂CO₂H (82) | 492 |
| | n-C₇H₁₅CH=CH₂ | Peroxide | n-C₇H₁₅CH₂CH₂SCH(CO₂H)CH₂CO₂H (84) | 492 |
| HSCH₂CO₂CH₂CH₂OCOCH₂SH | (CH₃)₂CHCH₂CH₂CH=CH₂ | None added | Polymer (—) | 479 |
| | ClSi(CH₃)₂CH=CH—CH₃ | None added | Polymer (—) | 479 |

† No structures was given for this product.

## TABLE X—Continued

### C. Addition of Aliphatic Dithiols to Olefins
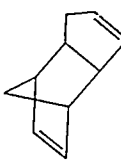
| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HSCH₂CH₂SH | CHCl=CH₂ | Phenyl disulfide + UV | Cl(CH₂)₂S(CH₂)₂S(CH₂)₂Cl (100) | 187 |
| | HOCH₂CH=CH₂ | Peroxide + UV | HO(CH₂)₃SCH₂CH₂S(CH₂)₃OH (56) | 494 |
| | $CH_2=\overset{\displaystyle C}{\underset{\displaystyle O=C-O}{|}}-\overset{\displaystyle C}{\underset{\displaystyle }{|}}=CH_2$ | Azonitrile + UV | $CH_2-CHCH_2S(CH_2)_2SCH_2CH-CH_2$ ($O=C-O$) (89) | 181 |
| | CH₂=CHCH=CH₂ CH₂=CH(CH₂)₂CH=CH₂ | UV UV | Polymer (mol. wt. = 1100) (40) (C₈H₁₆S₂)ₓ | 495 148 |
| | [4-vinylcyclohexene structure] CH=CH₂ | None added | Polymer (mol.wt. = 1060) (87) | 495 |
| | p-CH₃C₆H₄SCH=CH₂ | None added | p-CH₃C₆H₄S(CH₂)₂S(CH₂)₂-S(CH₂)₂SC₆H₄CH₃-p (—) | 447, 496, 497 |
| | [bridged bicyclic diene structure] | None added | C₁₀H₁₃SCH₂CH₂SC₁₀H₁₃ʹ (—) | 465 |
| HS(CH₂)₃SH | CH₂=CH(CH₂)₃CO₂H n-C₁₁H₂₃CH=CH₂ | None added Peroxide | HO₂C(CH₂)₁₀S(CH₂)₃S(CH₂)₁₀CO₂H (60) n-C₁₃H₂₅S(CH₂)₃SC₁₃H₂₇-n (—) | 498 67 |
| | [cyclohexene structure] | UV | [cyclohexyl–S(CH₂)₃S–cyclohexyl structure] (100) | 499 |
| | CH₂=CH(CH₂)₃CO₂H n-C₁₁H₂₃CH=CH₂ | None added Peroxide | HO₂C(CH₂)₁₀S(CH₂)₃S(CH₂)₁₀CO₂H (47) n-C₁₃H₂₅S(CH₂)₃SC₁₃H₂₇-n (—) | 498 67 |

TABLE X—Continued

C. Addition of Aliphatic Dithiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HS(CH₂)₆SH (contd.) | (cyclohexene)—CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ or UV | $(C_{14}H_{26}S_2)_x$ (100) | 501, 148 |
| | CH₂=CH(CH₂)₄CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ UV | $(C_{14}H_{28}S_2)_x$ (—) | 146 |
| | CH₂=C(CH₃)(CH₂)₂C(CH₃)=CH₂ | UV | $[S(CH_2)_6SCH_2CH(CH_3)\cdot(CH_2)_2CH(CH_3)CH_2]_x$ (94–100) | 148, 501 |
| | (CH₂=CHCH₂)₂Si(CH₃)₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[S(CH_2)_6S(CH_2)_3Si(CH_3)_2(CH_2)_3]_x$ (78–86) | 502 |
| | CH₂=CH(CH₂)₇CH=CH₂  CH₂=CH(CH₂)₈CO₂H | UV  None added | $(C_{17}H_{32}S_2)_x$ (—)  $HO_2C(CH_2)_{10}S(CH_2)_6S(CH_2)_{10}CO_2H$ (51) | 148  498 |
| | (benzene ring with CH₂CH=CH₂ and OH) | UV | $-[S(CH_2)_6S(CH_2)_3\text{—}C_6H_3(CH_3)_3(OH)]_x-$ (80–100) | 501 |
| | CH₂=CHC₁₁H₂₃-n | Peroxide | $n\text{-}C_{13}H_{27}S(CH_2)_6SC_{13}H_{27}\text{-}n$ (—) | 67 |
| | (benzene ring with CH₂CH=CH₂ and OCOCH₃) | UV | $-[S(CH_2)_6S(CH_2)_3\text{—}C_6H_3(CH_3)_3(OCOCH_3)]_n-$ (89–100) | 501 |
| | (CH₃CH=CHCH₂SCH₂CH₂CH₂)₂  (p-CH₂=CHCH₂C₆H₄)₂CH₂  [CH₂=CH(CH₂)₄]₂O | UV  UV  UV | Red gum (—)  $(C_{23}H_{30}S_2)_x$ (—)  Polymer$^o$ (80) | 146  148  146 |

| | | | | |
|---|---|---|---|---|
| HSCH₂CH₂SH | n C₅H₁₁·CH=CH₂ | Peroxide | n C₅H₁₁·CH₂S(CH₂)₂SC₅H₁₁ n (—) | 67 |
| | CH₂=CHCH₂CH₂CH=CH₂ <br> CH₂=CHCH₂—CH₂ | (NH₄)₂S₂O₈ + CoSO₄ | Polymer (90–95) | 118 |
| | CH₂=CH₂ | (NH₄)₂S₂O₈ + CoSO₄ | Polymer (72) | 118 |
| HS·CH₂·C₆H₄·SO₂·OC₆H₄·CH₃ n | CH₂=CHCOC₆H₅ <br> CH₂=CHCO·C₆H₄·CH₃ n | Peroxide Ascaridole | C₆H₅·(OC₆H₄·SO₂C₆H₄·OCH₃ (88) <br> C₆H₅(OC₆H₄SO₂C₆H₄OCC₆H₄ n (89) | 195, 195 |
| HS(CH₂)₃·SH <br> [(HSCH₂)₂S(CH₃)₂] | CH₂=CH·C₆H₁₃ n <br> C₆H₅·CH=CHCH₂·CH₃ | Peroxide (NH₄)₂S₂O₈ + NaHSO₃ CoSO₄ | n·C₆H₁₃S(CH₂)₃SC₆H₁₃ n (—) <br> [(C₆H₅·CH(CH₃)·CH₂CH₂)₂S] (87) | 87, 502 |
| | (CH₂=CHCH₂)₂CHOH | UV | [(CH₃)₂·CHOH·CH₂·S(CH₂)₂S(CH₂)₃·(CH₃)₂SₓSᵧ (69–83)] | 502 |
| | | | [CH₂·CH(CH₃)·(CH₂)₃·CH(CH₃)·CH₂ <br> OH | 502 |
| | CH₂=CHCH₂·(CH₂)₂CH₂—CH₂ | UV | [(CH₂·CH(CH₃)·(CH₂)₃·CH(CH₃)·CH₂ <br> S(CH₂)₂S(CH₂)₃SₓSᵧ (81–84)] <br> [(CH₂)₄S·(CH₂)₂S·(CH₂)₃SₓSᵧ (79–83)] | 502 |
| | CH₂=CHCH₂·CH=CH—CH₃ | UV | [(CH₂)₄S(CH₂)₂S(CH₂)₃S(CH₂)₃Sₓ <br> OH ](77–79) | 502 |
| | CH₂=CHCH₂ <br> OH | UV | [(CH₂)₄S(CH₂)₂S(CH₂)₃SₓSᵧ <br> OOCCH₃ ](81–84) | 502 |
| | CH₂=CHCH₂ <br> OOCCH₃ | UV | | 502 |

Note: References 385 to 631 are on pp 371–378

*The structure and empirical formula were not determined

TABLE X—Continued

C. Addition of Aliphatic Dithiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| HS(CH₂)₆SH | $CH_2=CHC_{11}H_{23}$-$n$ | Peroxide | $n$-$C_{13}H_{27}S(CH_2)_6SC_{13}H_{27}$-$n$ (—) | 67 |
| | $CH_2=CHCH=CH_2$ | UV | Polymer (50) | 495 |
| | $CH_2=CH(CH_2)_2CH=CH_2$ | UV | $(C_{16}H_{32}S_2)_x$ (—) | 148 |
| HS(CH₂)₁₀SH | (ring)—$CH=CH_2$ | UV | Polymer (mol. wt. 1180) | 495 |
| | $CH_2=CH(CH_2)_7CH=CH_2$ | UV | $(C_{21}H_{42}S_2)_x$ (—) | 148 |
| | $CH_2=CHC_{11}H_{23}$-$n$ | Peroxide | $n$-$C_{13}H_{27}S(CH_2)_{10}SC_{13}H_{27}$-$n$ (—) | 67 |
| (CH₃-cyclohexene-SH) | $CH_3C=CH_2$ (+-Limonene) | $(NH_4)_2S_2O_8$ + $CuSO_4$ | Polymer (92) | 118 |
| [HS(CH₂)₃Si(CH₃)₂]₂O | $CH_2=CH(CH_2)_2CH=CH_2$ | UV | $[(CH_3)_2Si(CH_2)_3Si(CH_3)_2OSi(CH_3)_3(CH_2)_3S]_x$ (83) | 502 |
| | $CH_2=C(CH_3)(CH_2)_2C(CH_3)=CH_2$ | UV | $[CH_3CH(CH_2)_3CH(CH_3)_2CH(CH_3)CH_2S(CH_3)_3Si(CH_3)_2OSi(CH_3)_3(CH_2)_3Si]_x$ (81) | 502 |
| | $(CH_2=CHCH_2)_2Si(CH_3)_2$ | UV | $[(CH_3)_2Si(CH_2)_3Si(CH_2)_3S(CH_2)_3Si(CH_3)_2OSi(CH_3)_2(CH_2)_3S]_x$ (—) | 502 |
| HS(CH₂)₁₁SH | $CH_2=CHC_{11}H_{23}$-$n$ | Peroxide | $n$-$C_{13}H_{27}S(CH_2)_{11}SC_{13}H_{27}$-$n$ (—) | 67 |
| HS(CH₂)₁₂SH | $CH_2=CHC_{11}H_{23}$-$n$ | Peroxide | $n$-$C_{13}H_{27}S(CH_2)_{12}SC_{13}H_{27}$-$n$ (—) | 67 |
| ($p$-HSCH₂C₆H₄CH₂)₂CH₂ | ($p$,$CH_3=CHC_6H_4)_2CH_2$ | UV | $(C_{23}H_{30}S_2)_x$ (—) | 148 |
| HS(CH₂)₁₈SH | $CH_2=CHC_{11}H_{23}$-$n$ | UV | $(C_{31}H_{56}S_2)_x$ (—) | 148 |
| | | Peroxide | $n$-$C_{13}H_{27}S(CH_2)_{18}SC_{13}H_{27}$-$n$ (—) | 67 |

## TABLE X—Continued

### D. Addition of Aromatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5SH$ (contd.) | $CH_2$=CHCH(CH$_3$)$_2$ | None added | $C_6H_5S(CH_2)_2CH(CH_3)_2$ (80) | 68 |
| |  | UV |  (cis) (49) | 92, 97 |
| |  | UV |  (93) $(C_6H_5)_2S_2$ | 103, 168 |
| | $CH_2$=CHC$_4$H$_9$-n | Peroxides + FeCl$_2$ | $C_6H_5SC_6H_{13}$-n (32) | 177, 437, 138 |
| | $CH_2$=CHOC$_4$H$_9$-n | None added | $C_6H_5SCH_2CH_2OC_4H_9$-n (90–96) $C_6H_5SCH(CH_3)OC_4H_9$-n (3–5) | 112 |
| |  | None added |  (?)  (?) | 103 |

| | | | References |
|---|---|---|---|
|  | Persulfate | $CH_3$ / $SC_2H_5$ (50) | 108, 114, 466 |
|  | None added |  $SC_2H_5$ (72) | 141 |
|  $CH_2=CHC_6H_5$ / $CH_3-CHSC_9H_{15}$ / $CH_2=C(SO)_2C_6H_5$ / $CH_2=CHSO_2C_4H_{15}$ | UV / None added / None added / None added |  $O_2$ $SC_2H_5$ / $C_6H_5SCH_2CH_2C_6H_5$ (90) / $C_6H_5SCH_2CH(CH_3)C_6H_5$ (100) / $C_6H_5SC_6H_2C_6H_5SO_2C_4H_5$ (94) / $C_6H_5SCH_2CH_2S(OC_2H_5)_2$ (75) | 64, 63 / 443 / 141 / 472 |
|  | None added |  $SC_2H_5$ (80) | 461 |
|  $CH_2=CHC_4H_9$ / $CH_3CHO_2CH_2CH_4$ / $CH_2=C(CH_3)CHO_2CH_3$ / $C_6H_5COCH=CHCO_2H$ / $C_6H_5CH=CHCH=CH_2$ | None added / Aromatic / Aromatic / None added / None added | $C_6H_5SCH_2CH(CH_3)C_4H_9$ [a] / $C_6H_5SCH(CH_3)CH_2SC_2H_4$ (82) / $C_6H_5SCH(CH_2)CHO_2CH_3$ (82) / $C_6H_5COCH_2CH(CH_2)HSC_6H_5$ [—] / $C_6H_5CH_2=CHCH=CHSC_6H_5$ [a] | 63 / 449 / 448 / 122 / 63 |
|  | None added |  $SC_2H_5$ [a] | 63 |
|  $3,4\ CH_2O_2C_6H_3CH_2CH_2CH=CH_2$ | Peroxide | $3,4\ CH_2O_2C_6H_3SC_4H_9$ [—] | 438 |

*Note:* References 385 to 631 are on pp. 371–374.

[a] The product was isolated as the sulfone.

TABLE X—*Continued*

D. *Addition of Aromatic Thiols to Olefins—Continued*
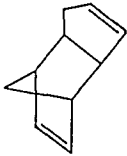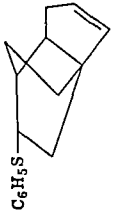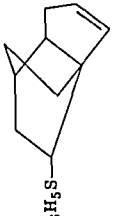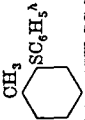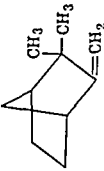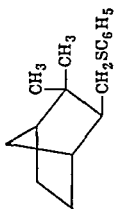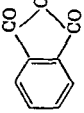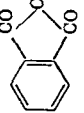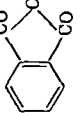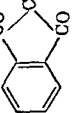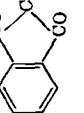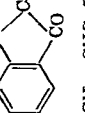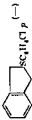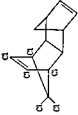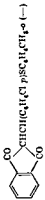
| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|

C₆H₅SH (*contd.*)



None added



(93)

465

$CH_3C=CH_2$
(— -Limonene)

None added



(—)

63



(Camphene)

None added



(—)

63

TABLE X—Continued

D. Addition of Aromatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5SH$ (contd.) | (indandione) $C=CHC_6H_4NO_2\text{-}o$ | None added | (indandione) $CHCH(SC_6H_5)C_6H_4NO_2\text{-}o$ (—) | 136 |
| | (indandione) $C=CHC_6H_4NO_2\text{-}m$ | None added | (indandione) $CHCH(SC_6H_5)C_6H_4NO_2\text{-}m$ (—) | 136 |
| | (indandione) $C=CHC_6H_4NO_2\text{-}p$ | None added | (indandione) $CHCH(SC_6H_5)C_6H_4NO_2\text{-}p$ (—) | 136 |
| | (indandione) $C=CHC_6H_5$ | None added | (indandione) $CHCH(C_6H_5)SC_6H_5$ (—) | 136 |
| | (indandione) $C=CHC_6H_4CH_3\text{-}m$ | None added | (indandione) $CHCH(SC_6H_5)C_6H_4CH_3\text{-}m$ (—) | 136 |
| | (indandione) $C=CHC_6H_4CH_3\text{-}p$ | None added | (indandione) $CHCH(SC_6H_5)C_6H_4CH_3\text{-}p$ (—) | 136 |
| | $CH_2=CHC_{15}H_{31}\text{-}n$ | Peroxide | $C_6H_5SC_{17}H_{35}\text{-}n$ (—) | 67 |
| | $CH_2=CHC_{17}H_{35}\text{-}n$ | Peroxide | $C_6H_5SC_{19}H_{39}\text{-}n$ (—) | 67 |
| | Squalene | Peroxide + UV | Nature of product not investigated. | 108 |

| | | | |
|---|---|---|---|
| $p$ ClC$_6$H$_4$SH | UV | $SC_6H_4Cl$-$p$ $^{ca}$ (—) + ($p$ ClC$_7$H$_{12}$S)$_x$ (—) | 92 |
| | UV | $SC_6H_4Cl$-$p$ $^{ca}$ (—) + ($p$-ClC$_7$H$_{13}$S)$_x$ (—) | 92 |
| | None added | $SC_6H_4Cl$-$p$ (—) | 461 |
| | None added | $p$ ClC$_6$H$_4$S (103) | 166 |
| | UV or Peroxide | $SC_6H_4Cl$-$p$ (3) | 166 |
| $o$ CH$_3$C$_6$H$_4$SH | None added | CHCHC$_6$H$_4$Cl $p$)$SC_6H_4Cl_4$-$o$ (—) | 135 |
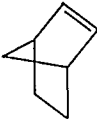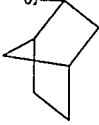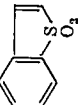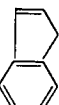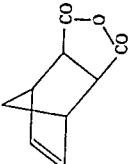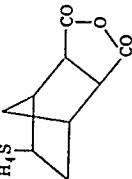
*Note:* References 385 to 631 are on pp. 371–376.

TABLE X—*Continued*

D. *Addition of Aromatic Thiols to Olefins—Continued*

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| o-CH₃C₆H₄SH (contd.) | (structure) C=CHC₆H₄NO₂-o | None added | (structure) CHCH(C₆H₄NO₂-o)SC₆H₄CH₃-o (—) | 136 |
| | (structure) C=CHC₆H₄NO₂-m | None added | (structure) CHCH(C₆H₄NO₂-m)SC₆H₄CH₃-o (—) | 136 |
| | (structure) C=CHC₆H₄NO₂-p | None added | (structure) CHCH(C₆H₄NO₂-p)SC₆H₄CH₃-o (—) | 136 |
| | (structure) C=CHC₆H₅ | None added | (structure) CHCH(C₆H₅)SC₆H₄CH₃-o (—) | 136 |
| | (structure) C=CHC₆H₄CH₃-p | None added | (structure) CHCH(C₆H₄CH₃-p)SC₆H₄CH₃-o (—) | 136 |
| 2-CH₃-4-ClC₆H₃SH | CH₂=CHSO₂C₆H₄CH₃-p | None added | 2-CH₃-4-ClC₆H₃SCH₂CH₂SO₂C₆H₄CH₃-p (—) | 447, 506, 507 |
| m-CH₃C₆H₄SH | CH₂=C(CH₃)CO₂CH₃ | UV | m-CH₃C₆H₄SCH₂CH(CH₃)CO₂CH₃ (45) m-CH₃C₆H₄SC(CH₃)(CO₂CH₃)(CH₂)₂-CH(CH₃)CO₂CH₃ᶜ (11) | 91 |

| | | |
|---|---|---|
| $p$-$CH_3C_6H_4SH$ | | |
| $CH_2$=$CHCH$=$CH_2$ | UV | $p$-$CH_3C_6H_4S(CH_2)_4SC_6H_4CH_3$-$p$ (39) | 148 |
| | Peroxide | $p$-$CH_3C_6H_4SCH_2CH$=$CHCH_3$ (trans) (90) | 147, 149 |
| $CH_2$=$CHC_6H_4$-$CH_3$ | None added | $p$-$CH_3C_6H_4S(CH_2)_2C_6H_4CH_3$ (—) | 447 |
| $CH_2$=$CHSC_2H_4$ | UV | ~C~H~ (—) | 92 |
|  | UV |  | 91 |
| $CH_2$=$CHCH_2CO_2CH_3$ | UV | $p$-$CH_3C_6H_4SCH_2CH(CH_3)CO_2CH_3$ [78] | 150a |
| | UV | $p$-$CH_3C_6H_4SCH_2CH_2CH_2CO_2CH_3$ (14) | |
| | UV | $CHCH_3(CO)_2CH_3$ | |
| $CH_2$=$CHCO$=$CCH$=$CH_2$ | UV | $p$-$CH_3C_6H_4S(CH_2)_4[SC_6H_4CH_3-p]_2SC_2H_4SC_6H_4CH_3$-$p$ (60) | 92 |
|  | None added | ~C~H~ (—) | 479 |
| $CH_2$=$CHC_6H_4$-$CH_3$ | Peroxide | $p$-$CH_3C_6H_4SCH_2C_6H_4S(CH_3)_3$ (96) | 435, 109 |
|  | None added | $SC_6H_4CH_3$-$p$  (98) | 103 |
|  | | $SC_6H_4CH_3$-$p$  (98) | |
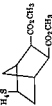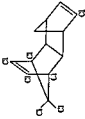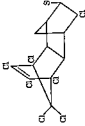
Note: References 385 to 631 are on pp. 311-376.
† The structure was not proved.

## TABLE X—Continued

### D. Addition of Aromatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $p$-CH$_3$C$_6$H$_4$SH (contd.) | (norbornene) | None added | (bicyclic) SC$_6$H$_4$CH$_3$-$p$ (56) | 100 |
| | (methylenecyclohexadiene, =CH$_2$) | None added | CH$_2$SC$_6$H$_4$CH$_3$-$p$ (81) | 147 |
| | (benzothiophene S, O$_2$) | None added | SC$_6$H$_4$CH$_3$-$p$, S, O$_2$ (85) | 141 |
| | (dimethylenecyclohexane, =CH$_2$ =CH$_2$) | None added | CH$_2$SC$_6$H$_4$CH$_3$-$p$, CH$_3$ (88) | 147 |
| | (indene) | None added | SC$_6$H$_4$CH$_3$-$p$ (90) | 461 |
| | (cyclopropane-fused bicyclic, CO-O-O-CO) | None added | $p$-CH$_3$C$_6$H$_4$S, CO-O-O-CO (73) | 101 |

| | | | |
|---|---|---|---|
| $CH_2=CHSC_6H_4CH_3, p$ | None added | $p\text{-}CH_3C_6H_4SCH_2CH_2SC_6H_4CH_3, p$ (—) | 447, 406, 497 |
| $CH_2=CHSO_2C_6H_4CH_3 p$ | None added | $p\text{-}CH_3C_6H_4SCH_2CH_2SO_2C_6H_4CH_3, p$ (—) | 447, 506, 507 |
| $C_6H_5CH=CHCOOC_2H_5$ | None added | $p\text{-}CH_3C_6H_4SCH(C_6H_5)CH_2COOC_2H_5$ (—) | 123 |
| $3,4\text{-}CH_2O_2C_6H_3CH=CHCH_3$ | Peroxide | $3,4\text{-}CH_2O_2C_6H_3CH(CH_3)CH(SC_6H_4CH_3)C_6H_5, p$ (—) | 436 |



$p\text{-}CH_3C_6H_4S$ (32)

101



None added    $p\text{-}CH_3C_6H_4SC_{10}H_{16}\,n$ (—)    67

Peroxide    447, 406, 497



None added    $SC_6H_4CH_3, p$ (80)    102

TABLE X—Continued

D. Addition of Aromatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $p\text{-}CH_3C_6H_4SH$ (contd.) | $CH_2=CHC_{11}H_{23}\text{-}n$ | Peroxide | $p\text{-}CH_3C_6H_4SC_{13}H_{27}\text{-}n$ (—) | 67 |
| | $C_6H_5CH=CHCOC_6H_4NO_2\text{-}p$ | None added | $p\text{-}CH_3C_6H_4SCH(C_6H_5)CH_2COC_6H_4NO_2\text{-}p$ (85) | 124 |
| | $C_6H_5CH=CHCOC_6H_5$ | None added | $p\text{-}CH_3C_6H_4SCH(C_6H_5)CH_2COC_6H_5$ (—) | 123 |
| | $CH_2=CHC_{13}H_{27}\text{-}n$ | Peroxide | $p\text{-}CH_3C_6H_4SC_{15}H_{31}\text{-}n$ (—) | 67 |
| | phthalide $C=CHC_6H_4Cl\text{-}p$ | None added | $CHCH(C_6H_4Cl\text{-}p)SC_6H_4CH_3\text{-}p$ (—) | 136 |
| | phthalide $C=CHC_6H_4NO_2\text{-}o$ | None added | $CHCH(C_6H_4NO_2\text{-}o)SC_6H_4CH_3\text{-}p$ (—) | 136 |
| | phthalide $C=CHC_6H_4NO_2\text{-}m$ | None added | $CHCH(C_6H_4NO_2\text{-}m)SC_6H_4CH_3\text{-}p$ (—) | 136 |
| | phthalide $C=CHC_6H_4NO_2\text{-}p$ | None added | $CHCH(C_6H_4NO_2\text{-}p)SC_6H_4CH_3\text{-}p$ (—) | 136 |
| | phthalide $C=CHC_6H_5$ | None added | $CHCH(C_6H_5)SC_6H_4CH_3\text{-}p$ (—) | 136 |

102

163

136



$p$-CH$_3$C$_6$H$_4$S—

(73)

SC$_6$H$_4$CH$_3$-$p$

(19)

SC$_6$H$_4$CH$_3$, $p$ (—)

$m$)SC$_6$H$_4$CH$_3$-$p$ (—)

None added

Peroxide

None added

C$_7$H$_6$O

C$_7$H$_6$O

=CHCH$_2$C$_6$H$_4$CH$_4$-m

## TABLE X—Continued

### D. Addition of Aromatic Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| p-CH₃C₆H₄SH (cont'd.) | (phthalide-type structure, =C—CHC₆H₄CH₃-p) | None added | (structure) ClCHCH(C₆H₄CH₃-p)SC₆H₄CH₃-p (—) | 136 |
| | CH₂=CHC₁₅H₃₁-n | Peroxide | p-CH₃C₆H₄SC₁₇H₃₅-n (—) | 67 |
| | CH₂=CHC₁₆H₃₃-n | Peroxide | p-CH₃C₆H₄SC₁₆H₃₃-n (—) | 67 |
| (dimethyl-substituted benzene thiol: CH₃, SH, CH₃) | CH₂=CHSC₂H₅ | None added | (structure: Cl, CH₃ benzene) SCH₂CH₂SC₂H₅ | 447, 496, 497 |
| p-C₆H₅C₆H₄SH | CH₂=CHC₄H₉-n | Peroxide | p-C₆H₅C₆H₄SC₆H₁₃-n (—) | 507b |
| | CH₂=CHC₅H₁₁-n | Peroxide | p-C₆H₅C₆H₄SC₇H₁₅-n (—) | 507b |
| | C₆H₅CH=CH₂ | Peroxide | p-C₆H₅C₆H₄SCH₂CH₂C₆H₅ (—) | 507b |
| | CH₂=CH(CH₂)ₙCH₃  n = 5–14 | Peroxide | p-C₆H₅C₆H₄S(CH₂)ₙCH₃ (—)  n = 7–16 | 507b |
| (2-vinylpyridine structure: N—CH=CH₂) | | UV | β-C₁₀H₇SCH₂CH(CH₃)CO₂CH₃ (41) + higher-boiling material | 91 |
| | (indene structure) | None added | β-C₁₀H₇SCH₂CH₂SC₁₀H₇-β (41) | 109 |
| (2-naphthalenethiol structure: SH) | CH₂=CHSC₆H₄CH₃-p | None added | (indane structure) SC₁₀H₇-β (91) | 461 |
| | CH₂=CH(CH₂)₈CO₂H | UV | β-C₁₀H₇SCH₂CH₂SC₆H₄CH₃-p (—) | 447, 496 |
| | | | β-C₁₀H₇S(CH₂)₁₀CO₂H (—) | 450 |
| | CH₂=CH(CH₂)ₙCH₃  n = 8, 10, 12, 14, 16 | Peroxide | β-C₁₀H₇S(CH₂)ₙCH₃ (—)  n = 10, 12, 14, 16, 18 | 67 |

| | | | | |
|---|---|---|---|---|
| Cl (naphthalene) | $CH_2=CHSO_2C_6H_4CH_3,p$ | None added | Cl (naphthalene) $SCH_2CH_2SO_2C_6H_4CH_3,p$ | 447, 506, 507 |
| 611 | | | | |
| anthraquinone, SH | $CH_2=CHSO_2C_6H_4CH_3,p$ | None added | anthraquinone $SCH_2CH_2SO_2C_6H_4CH_3,p$ | 447, 506, 496, 497 |
| | $CH_2=CHSO_2C_6H_4CH_3,p$ | None added | anthraquinone $SCH_2CH_2SO_2C_6H_4CH_3,p$ | 447 |
| anthracene, SH | $CH_2=CHSC_6H_4CH_3,p$ | None added | anthraquinone $SCH_2CH_2SC_6H_4CH_3,p$ | 447, 496, 506, 497 |
| | $CH_2=CHSO_2C_6H_4CH_3,p$ | None added | anthraquinone $SCH_2CH_2SO_2C_6H_4CH_3,p$ | 447 |

## TABLE X—Continued

### E. Addition of Aromatic Dithiols to Olefins

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| m-HSC₆H₄SH | CH₂=CHCH=CH₂ | UV | Polymer[a] (75) | 495 |
| | CH₂=CHO(CH₂)₂OCH=CH₂ | UV | Polymer[a] (—) | 495 |
| |  CH=CH₂ | UV | Polymer[a] (—) | 495 |
| p-HSC₆H₄SH | CH₂=CH(CH₂)₂CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[-S-C_6H_4-S(CH_2)_6-]_x$ (75) | 152 |
| (p-HSC₆H₄)₂ | CH₂=CH(CH₂)₂CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[-S-C_6H_4-C_6H_4-S(CH_2)_6-]_x$ (73) | 152 |
| (p-HSC₆H₄)₂CH₂ | CH₂=CH(CH₂)₂CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[-S-C_6H_4-CH_2-C_6H_4-S(CH_2)_6-]_x$ (82) | 152 |
| (p-HSC₆H₄)₂O | CH₂=CH(CH₂)₂CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[-S-C_6H_4-O-C_6H_4-(CH_2)_6-]_x$ (93) | 152 |
|  (naphthalene-dithiol) | CH₂=CH(CH₂)₂CH=CH₂ | (NH₄)₂S₂O₈, NaHSO₃ + CuSO₄ | $[-S-\text{(naphthalene)}-S(CH_2)_6-]_x$ (88) | 152 |

## F. Oxidative Addition of Thiols to Olefins

| | | | | |
|---|---|---|---|---|
| SH, HS (naphthalene) | $CH_2$=$CH(CH_2)_9CH$=$CH_2$ | $(NH_4)_2S_2O_8$ + $CuSO_4$ | [S(CH2)... naphthalene] (78) | 152 |
| SH, HS (naphthalene) | $CH_2$=$CH(CH_2)_9CH$=$CH_2$ | $(NH_4)_2S_2O_8$ + $CoSO_4$ | [S(CH2)... naphthalene] (85) | 152 |
| $HSCH_2CO_2H$ | anthracene + $O_2$ | None added | $SCH_2CO_2H$ / $SCOCH_3$ (—) | 169 |
| $CH_3COSH$ | anthracene + $O_2$ | None added | $SCOCH_3$ (2 isomers) (9 $C_{21}H_{14}S$) (—) | 169, 187 |
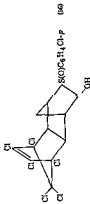
*Note:* References 385 to 631 are on pp. 371–376.

* The structure and empirical formula were not determined.
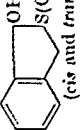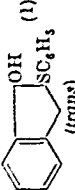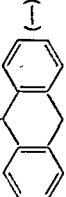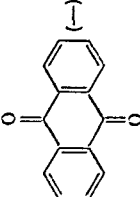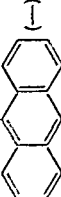
## TABLE X—Continued

### F. Oxidative Addition of Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| CH₃COSH (contd.) | 9,10-dimethylanthracene | O₂ | (anthracene) CH₃, SCOCH₃ (81) | 167 |
| | 9,10-diethylanthracene | O₂ | (anthracene) C₂H₅, SCOCH₃ (—) | 167 |
| $n$-C$_3$H$_7$SH | CH₂=CHC₆H₁₃-$n$ + O₂ | None added | $n$-C$_3$H$_7$CH$_2$S(O)CH$_2$CHOHC$_6$H$_{13}$-$n$ (27)<br>$n$-C$_3$H$_7$SC$_8$H$_{17}$-$n$ (6) | 111 |
| | C₆H₅CH=CH₂ + O₂ | None added | $n$-C$_3$H$_7$SCH$_2$CHOHC$_6$H$_{13}$-$n$ (5)<br>$n$-C$_3$H$_7$S(O)CH$_2$CHOHC$_6$H$_5$ (87)<br>$n$-C$_3$H$_7$S(CH$_2$)$_2$C$_6$H$_5$ (1)<br>($n$-C$_3$H$_7$)$_2$S$_2$ (1) | 111 |
| (CH₃)₂CHCH₂SH | CH₂=CHC₄H₉-$n$ + O₂ | Di-$t$-butyl diperoxalate | (CH$_3$)$_2$CHCH$_2$SC$_6$H$_{13}$-$n$ (14)<br>(CH$_3$)$_2$CHCH$_2$SO$_2$C$_6$H$_{13}$-$n$ (19)<br>(CH$_3$)$_2$CHCH$_2$SCH$_2$CHOHC$_4$H$_9$-$n$ (42) | 165, 508 |
| (CH₃)₃CSH | C₆H₅CH=CH₂ + O₂ | α-Cumyl hydroperoxide + FeSO₄ | C$_6$H$_5$CHOHCH$_2$S(O)C(CH$_3$)$_3$ (28) | 111 |
| | C₆H₅CH=CH₂ + O₂ | Dibutylamine hydrochloride | C$_6$H$_5$(CH$_2$)$_2$SC(CH$_3$)$_3$ (10)<br>C$_6$H$_5$CHO (19) | 162 |
| | C₆H₅CH=CH₂ + O₂ | None added | C$_6$H$_5$CHOHCH$_2$S(O)C(CH$_3$)$_3$ (36) | 159 |
| $p$-ClC₆H₄SH | C₆H₅CH=CH₂ + O₂ | None added | C$_6$H$_5$CHOHCH$_2$S(O)C$_6$H$_4$Cl-$p$ (—) | 159 |
| | indene + O₂ | None added | (indane) S(O)C$_6$H$_4$Cl-$p$, OH (—) | 159 |

| | | | |
|---|---|---|---|
| C₆H₅C(CH₃)=CH₂ + O₂ | None added | $p$-ClC₆H₄S(O)CH₂C(CH₃)(OH)C₆H₄Cl-$p$ (64) $p$-ClC₆H₄SCH₂C(CH₃)(OH)C₆H₅ (11–50) | 169 |
| (structure) endo or exo + O₂ | None added | $p$-ClC₆H₄SO (structure) (64) HO | 166 |
| (chlorinated structure) + O₂ | None added | S(O)C₆H₄Cl-$p$ (structure) OH (90) | 166 |
| CH₂=CHCN + O₂ | Dibutylamine hydrochloride | C₆H₅S(O)CH₂CHOHCN (50) | 162, 163 |
| CH₂=CHCH₂OCOCH₃ + O₂ | Dibutylamine hydrochloride | (structure) OH S(O)C₆H₅ (9) | 162 |
| C₆H₅CH=CH₂ + O₃ | None added | C₆H₅S(O)CH₂CHOHC₆H₅ (30) | 159 |
| C₆H₅CH=CH₂ + O₃ | Dibutylamine hydrochloride | C₆H₅CH₂CH(OOH)C₆H₅ (—) C₆H₅S(O)CH₂CHOHC₆H₅ (29) | 162 |

C₆H₅SH

## TABLE X—Continued

### F. Oxidative Addition of Thiols to Olefins—Continued
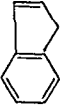
| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5SH$ (contd.) | (indane) $+ O_2$ | None added | OH / S(O)C₆H₅ (85) (cis and trans); OH / SC₆H₅ (1) (trans) | 157, 159 |
| | $C_6H_5C(CH_3){=}CH_2 + O_2$ | None added | $C_6H_5S(O)CH_2C(CH_3)(OH)C_6H_5$ / $C_6H_5SCH_2C(CH_3)(OOH)C_6H_5$ (52) | 159 |
| | (anthracene) $+ O_2$ | Peroxide + FeSO₄ | $(C_6H_5)_2S_2$ (—); (structure, SC₆H₅); (anthraquinone, O=...=O) | 169 |
| $C_6H_5COSH$ | (anthracene) $+ O_2$ | Peroxide + FeSO₄ | (structure, SCOC₆H₅) | 169 |

| | | | |
|---|---|---|---|
| $C_6H_5CH=CH_2$ $C_6H_5SH$ | | $SCOC_6H_5$ (2 isomers) $(-)$ | 162 |
| $CH_2=C(CH_3)CN + O_2$ | Dibutylamine hydrochloride | $(9\ C_6H_5)_5S\ (-)$ $C_6H_5CH_2S(O)CH_2CH_2CH(OH)C_6H_5\ (21)$ | 162 |
| | Dibutylamine hydrochloride | $p\text{-}CH_3C_6H_4S(O)CH_2CH_2CH(CN)C_6H_5\ (80)$ | 162 |
| $CH_2=CH(CO)_2CH_3 + O_2$ | Dibutylamine hydrochloride | $p\text{-}CH_3C_6H_4S(O)CH_2CH_2CHOHCO_2CH_3\ (34)$ | 162 |
| $CH_2=C(CH_3)CO_2CH_3 + O_2$ | Dibutylamine hydrochloride | $p\text{-}CH_3C_6H_4S(O)CH(CH_3)CHOHCO_2CH_3\ (24)$ | 162 |
| | Dibutylamine hydrochloride | $p\text{-}CH_3C_6H_4S(O)CH_2CH(CH_3)OHCO_2CH_3\ (95)$ | 162, 163 |
| $C_6H_5CH=CH_2$ | Dibutylamine hydrochloride | $p\text{-}CH_3C_6H_4S(O)CH(OH)CHOHC_6H_5\ (73)$ | 163 |
|  $+ O_2$ | None added | $S(O)C_6H_4CH_2^p\ (-)$ OH | 159 |
|  $+ O_2$ | None added | $\beta\text{-}C_{10}H_7S(O)CH_2CHOHC_6H_5\ (-)$ $SC_6H_4F\ \beta$ OH | 159 |
| | None added | $C_6H_5C(OOH)(CH_3)CH_2SC_6H_4F\ \beta\ (-)$ $S(O)C_6H_4F\ \beta\ (-)$ OH | 168, 159 |
| $C_6H_5C(CH_3)=CH_2$ | None added | $C_6H_5C(OH)(CH_3)CH_2S(O)C_6H_4F\ \beta\ (-)$ | 168, 159 |

## TABLE X—Continued

### F. Oxidative Addition of Thiols to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $n\text{-}C_{13}H_{27}SH$ | $C_6H_5CH=CH_2 + O_2$ | UV | $n\text{-}C_{13}H_{25}S(O)CH_2CHOHC_6H_5$ (75) (two isomers) | 159 |
| | indane $+ O_2$ | UV | $S(O)C_{13}H_{25}\text{-}n$ (31) OH (indane derivative) | 159 |
| | $C_6H_5C(CH_3)=CH_2 + O_2$ | UV | $n\text{-}C_{13}H_{25}S(O)CH_2C(CH_3)(OH)C_6H_5$ (10) | 159 |

### G. Addition of Thiol Acids to Olefins
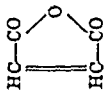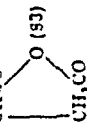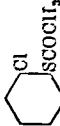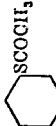
| Thiol Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| Monobasic $CH_3COSH$ | $CH_2=CHCl$ | Air | $CH_3COSCH_2CH_2Cl$ (51) | 178 |
| | $CH_2=CHF$ | $(n\text{-}C_4H_7)_2S_2$ + UV | $CH_3COSCH_2CH_2F$ (73) | 180 |
| | $CH_2=CBrCO_2H$ | None added | $CH_3COSCH_2CHBrCO_2H$ (67) | 125 |
| | $CH_2=CClCO_2H$ | None added | $CH_3COSCH_2CHClCO_2H$ (91) | 502, 125 |
| | $CH_2=CHCHO$ | Peroxide | $CH_3COSCH_2CH_2CHO$ (85) | 114, 125 |
| | $CH_2=CHCO_2H$ | None added | $CH_3COSCH_2CH_2CO_2H$ (72) | 125 |
| | $CH_2=CHCH_2Cl$ | None added | $CH_3COS(CH_2)_3Cl$ (79) | 510 |
| | $CH_2=CClCH_3$ | UV | $CH_3COSCH_2CHClCH_3$ (84) | 114, 511 |
| | $CH_2=CHCH_3$ | None added | Unidentified mixture | 88 |
| | $CH_2=CHCH_2OH$ | Peroxide | $CH_3COS(CH_2)_3OH$ (97) | 144 |
| | HC—CO / O / HC—CO | Peroxide | $CH_3COSCHCO$ — $CH_2CO$ O (93) | 144, 125 |
| | $HCO_2H$ / $=CHCO_2H$ | None added | $CH_3COSCHCO_2H$ / $CH_2CO_2H$ (83) | 125 |

| | | | |
|---|---|---|---|
| CH₂=CHOCOCH₃ | UV | CH₃COSCH₂CHClCOCH₃ (84) | 609, 612 |
| (CH₃)₂C=CHCHO | Peroxide | CH₃COSCH(CH₃)CH₂CHO (100) | 128, 144 |
| CH₂=CHCH₃ | None added | CH₃COSCH₂CH₂COCH₃ (83) | 139 |
| CH₂=CHCN | None added | CH₃COSCH₂CH₂CO₂H (87) | 126 |
| CH₂=C(CH₃)CH₂OH | None added | CH₃COSCH(CH₃)CO₂H (85) | 126 |
| CH₃O₂C·CH=CH₂ | Air | CH₃COSCH₂CH₂COCH₃ (102) | 513 |
| CH₃O₂C·CH=CH—CH₃ (trans) | UV | CH₃COSCH₂CH₂CH₂COCH₃ (109) | 178 |
| | | CH₃COSCH(CH₂CO₂H)CH₂CO₂H (57) | 25 |
| | | (9:1 threo, erythro) | |
| CH₃CH=CHCl (cis) | UV | CH₃COSCH(CH₃)CH₂CH₂Cl (88) | 25 |
| | | (0.3 erythro, erythro) | |
| CH₂=C(CH₃)₂ | None added | CH₃COSCH₂CH₂CH₂Cl (88) | 114, 511 |
| CH₂=C(CH₃)₂ | Peroxide | CH₃COSC(CH₃)₂CH₂OH (60) | 88 |
| CH₂=CHCH₂OH | Peroxide | CH₃COSCH₂CH₂CH₂OH (77) | 144 |
| CH₂=CH(CH₂)₄OCOCH₃ | | CH₃COSCH[(CH₂)₄OCOCH₃] (65) | 144 |
| | | CH₃COSCH₂CH[(CH₂)₂OCOCH₃] (15) | |
| CH₂=C(CO₂H)CH₂CO₂H (itaconic acid) | None added | CH₃COSCH₂C(CH₂CO₂H)CH₂CO₂H (—) | 136 |
| CHCO₂H ‖ CHCO₂H (maleic acid) | None added | CH₃COSCH(CO₂H)CH₂CO₂H (—) | 126 |
| CH₃OCH=CH—CH₃CHO | UV | CH₃COSCH₂CH(OCH₃)CH₂COCH₃ (100) | 127 |
| CH₃O₂C·CH=CH₂ | None added | CH₃COSCH₂CH(SCOCH₃)CO₂CH₃ (53) | 514, 516, 516 |
| (CH₃)₂CH=CHCHO | None added | CH₃COSCH₂CH₂CH₂CO₂CH₃ (83) | 148 |
| CH₃O₂C·CH—CHCO₂H | None added | CH₃COSCH(CO₂CH₃)CH₂CO₂H (85) | 129 |
| CH₃O₂C·CH=CHCO₂CH₃ | None added | CH₃COSCH(CO₂CH₃)₂CO₂H (86) | 129 |
| | None added | CH₃COSCH(CO₂H)CO₂H (66) | 129 |
| (CH₃)₂C=CHCO₂H | None added | CH₃COSC(CH₃)₂CH₂CO₂H (14) | 130 |
| | | CH₃COSC(CH₃)₂CH₂CO₂H (—) | 130 |

ᵈ The structure was not proved.

TABLE X—*Continued*

G. *Addition of Thiol Acids to Olefins—Continued*

| Thiol Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| Monobasic (contd.) | | | | |
| CH₃COSH (contd.) | CH₃CO₂CH₂CH=CH₂ | Peroxide | CH₃CO₂(CH₂)₃SCOCH₃ (100) | 144 |
| | CH₃OCH₂CH=CHCO₂H | None added | CH₃OCH₂CH(SCOCH₃)CH₂CO₂H (95) | 131 |
| | CH₂=CH(CH₂)₃Cl | UV | CH₃COS(CH₂)₅Cl (97) | 114, 511 |
| | CH₃CH=CHC₂H₅ (*cis* and *trans*) | UV | CH₃COSCH(CH₃)C₃H₇-*n* } (98) | 114 |
| | | UV | CH₃COSCH(C₂H₅)₂ } | 114 |
| | CH₂=C(CH₃)C₂H₅ | None added | CH₃COSCH₂CH(CH₃)C₂H₅ (52) | 88, 406 |
| | CH₃CH=C(CH₃)₂ | None added | CH₃COSCH(CH₃)CH(CH₃)₂ (87) | 88 |
| | CH₂=CHOH(CH₃)₂ | None added | CH₃COSCH₂CH(CH₃)₂ (80) | 445 |
| | CH₂=CHSi(CH₃)₃ | None added | CH₃COSCH₂Si(CH₃)₃ (67) | 517 |
| | CH₂=CHCH₂CH(CO₂H)₂ | None added | CH₃COS(CH₂)₃CH(CO₂H)₂ (59) | |
| | [3-chlorocyclohexene] | UV | [2-chloro-1-(SCOCH₃) cyclohexane] (84) (20% *trans*) | 97, 519 |
| | [4-methylcyclohexene] | None added or UV | [methylcyclohexyl SCOCH₃] (100) | 114, 112; 384, 408 |
| | [methylcyclopentene] | UV | [methyl-SCOCH₃ cyclopentane] (80) (*cis* and *trans*) | 98, 114 |
| | CH₂=CH(CH₂)₂CH=CH₂ | None added | CH₃COS(CH₂)₆SCOCH₃ (92) | 499, 519 |
| | CH₂=C(CH₃)C(CH₃)=C(CH₃)₂ | None added | CH₃COSCH₂C(CH₃)₂C(CH₃)=C(CH₃)₂ (89) or CH₃COSCH₂CH(CH₃)C(CH₃)=C(CH₃)₂ | 519 |
| | CH₂=CHCH₂CH₂COCH₃ | UV | CH₃COSCH₂CH(CH₃)C(CH₃)=CH₂ (91) | 518, 520 |
| | (CH₃)₃C=CHCOCH₃ | Peroxide | CH₃COS(CH₂)₄COCH₃ (91) | 521, 144 |
| | CH₃CO₂CH₂CH=CHC₂H₅ | Peroxide | CH₃COSC(CH₃)₂CH₂COCH₃ (92) | 144 |
| | CH₃CO₂CH₂C(CH₃)=CH₂ | None added | CH₃CO₂C₃H₆CH₂CH(CH₃)SCOCH₃ (74) | 99 |
| | | Peroxide | CH₃CO₂C₂H₄CH₂CH(C₂H₅)SCOCH₃ (72) | 144 |
| | | | CH₃CO₂CH₂CH(CH₃)CH₂SCOCH₃ (80) | |

| | | | |
|---|---|---|---|
| | CH₃CO₂CH₂CH=CHCH₃ | CH₃CO₂CH₂CH(CH₂)₂CH₃ •SCOCH₃ (75) | 99 |
| | C₂H₅CH₂(SCOCH₃)CH₂CH₂CH₂CH₂·̃ (—) | | 517 |
| | C₂H₅CH₂CH(CH₂)₂·CH₂CH₂CO₂C₂H₅ (—) | | 132 |
| | CH₃OCH=CH₂ ⁿ | (93) | 98, 114 |
| CH₃CO₂CH₂CH=CH₂ | | | 114 |
| (or) | CH₃CO₂CH[CH₂·]CH₂CH(CH₃)·ᵈ (94) | | |
| CH₃CH=CHOCOCH₃ | | | 114 |
| | CH₃CO₂CH[CH₂·]CH₂CH(CH₃)·ᵈ (93) | | |
| CH₃·CH=CHCH₂·ᵇ | | | 114, 384 |
| CH₃·—CH=CHCH(CH₃)·ᵇ | CH₃CO₂CH[CH₂·]CH₂CH·[CH₂·] (98) | | 114 |
| CH₃·—CO₂CH₂·ᵇ | CH₃CO₂SCH₂C₆H₅·ᵇ (95) | | 114, 384 |
| CH₃·CF=CCl₂·ᵇ | CH₃CO₂(CH₂)₂SiC₆H₅·ᵇ (96) | | 439 |
| CH₃=CHCH₂·Si(CH₃)₃·ᵇ | CH₃CO₂SiCH₂C₆H₅·ᵇ (79) | | 519 |
| CH₂=CHCH₂·Si(CH₃)₃·ᵇ | CH₃CO₂SCH[CH₂·]·Si(CH₃)₃C₆H₅·ᵇ (82) | | 445 |
| CH₂=CHCH₂·Si(CH₃)₃·ᵇ | CH₃COSC₄H₄·SiC₆H₅·ᵇ (79) | | 174 |
| (CH₂=CHCH₂CO₂CH₃)·ᵇ | CH₃COSC₄H₆·CHSOOCH₂·CH₂·COOCH₂·CO₂H (131) | | 522 |

| | | | |
|---|---|---|---|
| |  |  (85) | 98, 114, 112 |
| | (cis and trans) | | |

| | | | |
|---|---|---|---|
|  |  | | 523 |

| | | | |
|---|---|---|---|
| | (CH₃)₃CHₓNO₂·CO₂C₂H₅ | CH₃COSCₓ(CH₃)₂N₂·CO₂C₂H₅ (72) | 130 |
| | CH₃CO₂SₓCₓH₄(CO₂CH₃)·OOCH₃·ᵇ (79) | | 520 |
| CH₃·CH=CH₂·ᵇ | | | 445 |
| C₂H₅·CH=CH₂·ᵇ | CH₃COSC₄H·SiOCOCH₃·ᵇ (80) | | 99, 524, |
| CH₃·—COSC₄H₄·SiN(CH₃)₂·ᵇ | | | 445 |
| CH₃·CO₂SCH=CH₂·C₄H₄·ᵇ | CH₃COSCH₂CH₂·Si(CH₃)₂·C₄H₄·ᵇ (85) | | 445 |

Note. Reference 395 to 631 are on pp. 371–376.
ᵃ The structure was not proved.
ᵇ None added.
ᵉ The isomers were formed in about equal quantities.

## TABLE X—Continued

### G. Addition of Thiol Acids to Olefins—Continued

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|

**Thiol Acid**

**Monobasic (contd.)**

$CH_3COSH$ (contd.)

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| (cyclohexene with $CH=CH_2$) | None added | $CH_3COS$—(cyclohexyl)$CH=CH_2{}^q$ (18) | 118 |
| | | $CH_3CH_2SCOCH_3{}^q$ (26) | |
| (cyclohexene) | None added | $CH_3COS$—(cyclohexenyl)$CH_2CH_2SCOCH_3{}^q$ (30) | |
| (cyclohexenyl $OCOCH_3$) | None added | (cyclohexyl)$OCOCH_3$ (74) $SCOCH_3$ | 99 |
| $CHCO_2C_2H_5$ $\parallel$ $CHCO_2C_2H_5$ | None added | $C_2H_5OCOCH(SCOCH_3)CH_2CO_2C_2H_5$ (75) | 139 |
| $(CH_3)_2C=CH(CH_2)_2COCH_3$ | Peroxide | $(CH_3)_2CHCH(SCOCH_3)(CH_2)_2COCH_3$ (—) | 525 |
| $n$-$C_5H_7CH=C(CHO)C_2H_5$ | None added | $C_{10}H_{18}O_2S{}^r$ (52) | 521 |
| $(CH_3)_2C=CH(CH_2)_2COCH_3$ | None added | $(CH_3)_2CHCH(SCOCH_3)(CH_2)_2COCH_3$ (77) | 520 |
| $CH_3COSCH=CHC_6H_9$-$n$ | None added | $CH_3COSCH_2CH(SCOCH_3)C_6H_9$-$n$ (60) | 171 |
| $CH_2=CHC_8H_{13}$-$n$ | Peroxide | $CH_3COSC_8H_{17}$-$n$ (100) | 144, 526 |
| $CH_3CH=CHC_8H_{11}$-$n$ | Peroxide | $CH_3COSCH(CH_3)C_8H_{13}$-$n$ $CH_3COSCH(C_2H_5)C_7H_{11}$-$n$ } (100) | 144 |
| Diisobutylene [$CH_2=C(CH_3)CH_2$-$C(CH_3)_3$;$(CH_3)_2C=CHC(CH_3)_3$ 4:1] | None added | $CH_3COSCH_2CH(CH_3)CH_2C(CH_3)_3$ (87) + other isomers | 527 |
| $CH_2=CHCH_2CH(OC_2H_5)_2$ | UV | $CH_3COS(CH_2)_3CH(OC_2H_5)_2$ (52) | 518, 520 |
| $(CH_2=CHCH_2)_2Si(CH_3)_2$ | None added | $[CH_3COS(CH_2)_3]_2Si(CH_3)_2$ (79) | 502 |
| $CH_2=CHCH_2Si(CH_3)_2C_3H_7$-$n$ | None added | $CH_3COS(CH_2)_3Si(CH_3)_2C_3H_7$-$n$ (70) | 415 |

| | | | |
|---|---|---|---|
| CH₂=CHCH₂CH₂OH(CH₃)CH₂C₆H₅ | None added | CH₃COSC₄H₈C₆H₅(CH₃)C₆H₅ (81) | 445 |
| | Peroxide | CH₃COSC₄H₈CH₂CH₃CH₂CH₂CHO (90) | 144 |
| C₆H₅CH=CHCHO | None added | CH₃COSCH(CH)₂CH₂CO₂H (—) | 126 |
| C₆H₅C≡CH(CO)₂C₆H₅ | Peroxide | CH₃COSC₆H₅C₂H(CH₃)₂C₆H₅ (90) | 144, 384 |
| CH₃—CH₂—COCH₂C₆H₅ | | | |
| | None added | $\overset{C_9H_{17}}{\underset{N}{\bigvee}}CH_2CH_2SCOCH_3$ (24) | 833 |
| C₆H₅—CH₃ | | | |
| | None added | CH₃CO₂CH(CH₃COCH)C₃H₄ᵢ n (127) | 90 |
| CH₂OCH₂—CH₂C₆H₅ | None added | CH₃COSCH₂SₙC₆H₅C₄H₉ (85) | 445 |
| CH₂=CHCH—SₙC₆H₅ | None added | CH₃COS(CH₂)₂SₙC₁₀H₇α₁CH₃ (98) | 445 |
| CH₂=CHCH₂SₙC₁₀H₇-α₁CH₃ | | | |
| | None added |  (93) | 838 |
|  | | | |
| | UV | $\overset{CH_3}{\underset{}{\bigcirc}}$ Monothiol⁰ (17) | 118 |
| $\overset{CH_3}{\underset{}{\bigcirc}}$ (+ Limonene) | | CH₃CHCH₂SCOCH₃ | |
| C₆H₅CH₂—CHOOCH₃ | Peroxide | CH₃COSCH₂C₆H₅CH₂COCH₃ (90) | 144 |

Note: References 385 to 631 are on pp. 371–376.
f No structure was proved for the product.
g The structure was not proved.
h The position of the acetylthio group was not determined.

## TABLE X—Continued

### G. Addition of Thiol Acids to Olefins—Continued

| Thiol Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| Monobasic (contd.) | | | | |
| CH₃COSH (contd.) | $CH_3CH$=$CH_2$ (with OH, OCH₃ phenol structure) | Peroxide | OH, OCH₃ phenol structure; $CH_2CH_2CH_2SCOCH_3$ (78) | 141 |
| | (bicyclic structure with COC₂H₅, Cl, and alkene) | None added | (bicyclic structures with COC₂H₅, SCOCH₃, CH₃COS, H) (31) | 529 |
| | (bicyclic structure with COC₂H₅ and alkene) | None added | (bicyclic structure with COC₂H₅ᵠ, CH₃COS, H) (96) | 529 |
| | (α- + β-Pinene) with CH₃, CH₃, CH₃ | None added | $C_{12}H_{20}OS^f$ (60) | 519 |

| | | | |
|---|---|---|---|
| 98, 114 | 1,1 adduct$^d$ (70) | UV |  |
| 519 | $C_{11}H_{18}OS^f$ (72) | None added |  |
| 98, 114 | $C_{12}H_{18}OS^g$ (84) | UV |  |
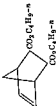
Note. References 385 to 631 are on pp. 371–376.
$^d$ No structure was given for this product.
$^g$ The position of the acetylthio group was not determined.

## TABLE X—Continued

### G. Addition of Thiol Acids to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| *Monobasic (contd.)* | | | | |
| CH₃COSH (contd.) | (bicyclic structure) CH₃, CH₃, =CH₂ (Camphene) | UV | (bicyclic structure) CH₃, CH₃, CH₂SCOCH₃ (77) | 98, 114, 519 |
| | CH₂=CHCO(CH₂)₄CO₂C₂H₅ | None added | CH₃COSCH₂CH₂CO(CH₂)₄CO₂C₂H₅ (91) | 133 |
| | (CH₃)₂C=CH(CH₂)₂C(CH₃)=CHCH₃ (Dihydromyrcene) | None added | (CH₃)₂CHCH(SCOCH₃)(CH₂)₂-CH(CH₃)CH(CH₃)SCOCH₃ʳ + (CH₃)₂C=CH(CH₂)₂CH(CH₃)CH(CH₃)SCOCH₃ʳ | 112 |
| | CH₂=C(CH₃) (ring with S) CH₃, C₂H₅ | UV | CH₃COSCH₂CH(CH₃) (ring with S) CH₃, C₂H₅ (—) | 529 |
| | (CH₃)₂C= (ring with S) CH₃, C₂H₅ | UV | CH₃COSC(CH₃)₂ (ring with S) CH₃, C₂H₅ (—) | 530 |
| | (CH₃)₂C=CH(CH(CH₃)₂)CH(CH₃)C₂H₅ | UV | (CH₃)₂CHCH(SCOCH₃)(CH₂)₂CH(CH₃)CH(CH₃)C₂H₅ (80) | 526 |
| | (CH₃)₂C=CH(CH₂)₂C(CH₃)(OH)C₂H₅ | None added | (CH₃)₂CH(SCOCH₃)(CH₂)₂C(CH₃)(OH)C₂H₅ (92) | 530 |
| | CH₂=CHCH₂Si(CH₃)₃ | None added | CH₃COS(CH₂)₃Si(CH₃)₃O (06) | 502 |
| | CH₃CO₂CH₂CH=CHC₆H₅ | Peroxide | CH₃CO₂CH₂CH₂CH(C₆H₅)SCOCH₃ (38) | 144 |
| | CH₂=CHCH₂Si(CH₃)₂C₆H₅ | None added | CH₃COS(CH₂)₃Si(CH₃)₂C₆H₅ (83) | 445 |
| | CH₂=CH(CH₂)₈CO₂H | Peroxide | CH₃COS(CH₂)₁₀CO₂H (85) | 456, 531 |
| | "Triisobutylene" | Peroxide | C₁₂H₂₅SCOCH₃ᶠ (39) | 527 |
| | CH₃=CH(CH₂)₈CO₂C₂H₅ | Peroxide | CH₃COS(CH₂)₁₀CO₂C₂H₅ (—) | 531 |
| | CH₂=CHC(C₆H₅)₂CH₃ | Peroxide | CH₃COSCH₂CH₂C(C₆H₅)₂CH₃ (95) | 463 |

| | | | |
|---|---|---|---|
| $CH_2=CHCH_2C_6H_5$-n | Peroxide | $CH_3COSC_6H_{13}$-n (75) | 144 |
| (p-$CH_3CON)_2CH_2CH_2C_6H_{13}C_6H_{13}CH_3$ (35) | UV | | 148 |
| | None added |  $CO_2C_4H_9$-n (—) | 528 |
| | | $CH_3CO_2$  | |
|  | Peroxide | $CH_3(CH_2)_{10}CH(SCOCH_3)(CH_2)_6CO_2H$ (—) | 531 |
| $CO_2C_4H_9$-n | UV | $CH_3(CH_2)_{10}CH(SCOCH_3)(CH_2)_8CO_2CH_3$ (70) | 532 |
| | None added | 'scous syrup | 112 |
| n-$C_4H_9CH=CH(CH_2)_7CO_2H$ (Oleic acid) | | | |
| n-$C_4H_9CH=CH(CH_2)_7CO_2CH_3$ (Methyl oleate) | | | |
| Squalene | | | |
| | None added |  SCOCH₂Cl (100) | 112 |
| | None added |  CH₃ SCOCH₂Cl (91) | 112 |
| $(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCH_3$ (Dihydromyrcene) | None added | CH₃C=CH(CH₂)₂CH(CH₃)CH(CH₃)· CH(CH₂)₂SCOCH₃ CH(CH₂)₂SCOCH₃ (70) | 112 |
| | | CH(CH₂)₂SCOCH₃CH(CH₃)· CH(CH₂)₂SCOCH₃ (—) | |
| Squalene | None added | 'scous syrup | 112 |
| ClCH₂COSH | | | |

*Note* References 285 to 531 are on pp. 371–376

<sup>e</sup> No structure was given for this product

<sup>f</sup> The relative yields of the two products depend upon the ratio of the starting materials

| | | | |
|---|---|---|---|
| $CH_2$=$CHC_nH_{2n}$-$n$<br>($p$-$ClC_6H_4CH_2CH_2C_6H_4CH_3$) | Peroxide<br>UV | $CH_3COSC_nH_{2n}$ $n$ (75)<br>($p$-$CH_3COSCH_2CH_2C_6H_4CH_2CH_3$) (38) | 144<br>148 |
|  | None added | $CH_3COS$  | 528 |
| | | | |
| | | | (−) |
| $n$ $C_2H_5CH$=$CH(CH_2)_xCO_2H$<br>(Oleic acid) | Peroxide | $CH_3(CH_2)_{8(?)}CH(SCOCH_3)(CH_2)_{7(8)}CO_2H$ (−) | 531 |
| $n$ $C_3H_7CH$=$CH(CH_2)_xCO_2CH_3$<br>(Methyl oleate) | UV | $CH_3(CH_2)_xCH(SCOCH_3)(CH_2)_xCO_2CH_3$ (70) | 532 |
| Squalene | None added | Viscous syrup | 112 |
| CClCH$_2$COSH | | | |
| | None added | $SCOCH_2Cl$ (100) | 112 |
|  | None added | $SCOCH_2Cl$ (91) | 112 |
| $(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=$CHCH_2$<br>(Dihydromyrcene) | None added | $(CH_3)_2C$=$CH(CH_2)_2CH(CH_3)$-<br>$CH(CH_3)SCOCH_2Cl$<br>$(CH_3)_2CHCH(SCOCH_2Cl)CH(CH_3)CH_2CH_3$ } (79)<br>$CH(CH_3)_2SCOCH_2Cl$ (−) | 112 |
| Squalene | None added | Viscous syrup | 112 |
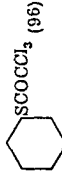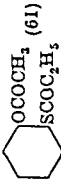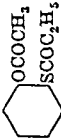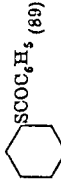
Note  References 365 to 631 are on pp. 371–376
$f$ No structure was given for this product
$g$ The relative yields of the two products depend upon the ratio of the starting materials

TABLE X—Continued

G. Addition of Thiol Acids to Olefins—Continued

| Thiol Acid | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| *Monobasic (contd.)* | | | | |
| $Cl_2CHCOSH$ | (cyclohexene) | None added | (cyclohexane)$SCOCHCl_2$ (96) | 112 |
| | $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_3$ (Dihydromyrcene) | None added | $(CH_3)_2C=CH(CH_2)_2CH(CH_3)$- $CH(CH_3)SCOCHCl_2$ (28) $(CH_3)_2CHCH(SCOCHCl_2)(CH_2)_2CH(CH_3)$- $CH(CH_3)SCOCHCl_2$ (2) | 112 |
| | Squalene | None added | Gum | 112 |
| $Cl_3CCOSH$ | (cyclohexene) | None added | (cyclohexane)$SCOCCl_3$ (96) | 112 |
| | (methylcyclohexene)$CH_3$ | None added | (cyclohexane)$CH_3$ $SCOCCl_3$ (100) | 112 |
| | $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_3$ (Dihydromyrcene) | None added | $(CH_3)_2C=CH(CH_2)_2CH(CH_3)CH(CH_3)SCOCCl_3$ (68) $(CH_3)_2CHCH(SCOCCl_3)(CH_2)_2CH(CH_3)$- $CH(CH_3)SCOCCl_3$ (trace) | 112 |
| $C_2H_5COSH$ | $CH_2=CHOCH_2CH(CH_3)_2$ | None added | $C_2H_5COSCH_2CH_2OCH_2CH(CH_3)_2$ (30) | 519 |
| | (cyclohexane)$OCOCH_3$ | None added | (cyclohexane)$OCOCH_3$ $SCOC_2H_5$ (61) | 99 |
| $C_6H_5COSH$ | (cyclohexene) | UV | (cyclohexane)$SCOC_6H_5$ (89) | 468 |
| *Divasic* | | | | |
| $HSCO(CH_2)_4COSH$ | $CH_2=CH(CH_2)_2CH=CH_2$ | UV | $[SCO(CH_2)_4COS(CH_2)_6]_x$ (72) | 153 |
| | (cyclohexene) | None added | (cyclohexane)$SCO(CH_2)_4COS$ (56) | 499 |

| Thiol | Olefin | Catalyst | Product | References |
|---|---|---|---|---|
| HSCO(CH$_2$)$_{14}$COSH | (CH$_2$=CH(CH$_2$)$_2$C(CH$_3$)=CHCH$_3$ (Dihydromyrcene) | None added |  ring CH$_3$, SCO(CH$_2$)$_{14}$COS$_-$ (84) | 499 |
| | Squalene | None added | Various gum | 499 |
| | | None added | Rubberg polymer | 499 |
| HSCO(CH$_2$)$_{14}$COSH | CH$_2$=CH(CH$_3$)CH=CH$_2$ | UV | [SCO(CH$_2$)$_{14}$]$_n$ (61) | 153 |
| HSCO(CH$_2$)$_{14}$COSH | CH$_2$=CH(CH$_2$)$_2$CH=CH$_2$ | UV | [SCO(CH$_2$)$_{14}$]$_n$ (69) | 153 |
| HSCO(CH$_2$)$_{14}$COSH | CH$_2$=CH(CH$_2$)$_2$CH=CH$_2$ | UV | [SCO(CH$_2$)$_{14}$]$_n$ (75) | 153 |
| HSCO(CH$_2$)$_{14}$COSH | CH$_2$=CH(CH$_2$)$_2$CH=CH$_2$ | UV | [SCO(CH$_2$)$_{14}$]$_2$ (92) | 153 |
| |  COSH | UV |  [SCO(CH$_2$)$_{14}$COS] (22) | 153 |
| HSCO(CH$_2$)$_{14}$COSH |  COSH | UV |  SCO(CH$_2$)$_{14}$COS (90) | 499, 633 |
| HSCO(CH$_2$)$_{14}$COSH |  COSH | UV |  [SCO(CH$_2$)$_{14}$COS] (66) | 153 |
| HSCO(CH$_2$)$_{14}$COSH |  CH$_3$ | UV |  ring CF$_3$, SCO(CH$_2$)$_{14}$COS (100) | 499, 633 |

## H. Addition of Thiol Phosphoric Acid Derivatives to Olefins

| Thiol | Olefin | Catalyst | Product | References |
|---|---|---|---|---|
| (CH$_3$O)$_2$P(S)SH | CH$_2$=CHCO$_2$CH$_3$ | None added | (CH$_3$O)$_2$P(S)SCH$_2$CH$_2$CO$_2$CH$_3$ (47) | 534, 134 |
| | CH$_2$=CHOOCCH$_3$ | None added | (CH$_3$O)$_2$P(S)SCH$_2$CH$_2$OOCCH$_3$ (69) | 534, 134 |
| | CH$_2$=CHCH$_2$OOCCH$_3$ | None added | (CH$_3$O)$_2$P(S)SCH(CH$_3$)CH$_2$CO$_2$CH$_3$ (38) | 534, 134 |
| | CH$_2$CO$_2$CH$_3$<br>$\,$<br>CHCO$_2$CH$_3$<br>(CH$_3$)$_2$C=CHCOCH$_3$ | None added | (CH$_3$O)$_2$P(S)S[CH(CO$_2$CH$_3$)CH$_2$CO$_2$CH$_3$] (34) | 134 |
| | | None added | (CH$_3$O)$_2$P(S)S[CH$_2$SCO(CH$_2$)$_{14}$CH$_2$OCOCH$_3$] (—) | 134 |

Note : References 386 to 631 are on pp. 371–376.

TABLE X—Continued

H. Addition of Thiol Phosphoric Acid Derivatives to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $(CH_3O)_2P(S)SH$ (cond.) | $CH_3CCO_2CH_3$<br>‖<br>$CHCO_2CH_3$ | None added | $CH_3CHCO_2CH_3$ (—)<br>│<br>$(CH_3O)_2P(S)SCHCO_2CH_3$ | 535 |
| | $CH_2{=}CHC_6H_5$ | None added | $(CH_3O)_2P(S)SCH_2CH_2C_6H_5$ (50) | 534, 134 |
| | $CHCO_2C_2H_5$<br>‖<br>$ClCCO_2C_2H_5$ | None added | $(CH_3O)_2P(S)SCHCO_2C_2H_5$ (28)<br>│<br>$ClCHCO_2C_2H_5$ | 535 |
| | $CHCO_2C_2H_5$<br>‖<br>$CHCO_2C_2H_5$ | None added | $(CH_3O)_2P(S)SCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ (50) | 534, 134 |
| | $CH_3CCO_2C_2H_5$<br>‖<br>$CHCO_2C_2H_5$ | None added | $CH_3CHCO_2C_2H_5$ (25)<br>│<br>$(CH_3O)_2P(S)SCHCO_2C_2H_5$ | 535 |
| | $CHCO_2C_3H_7\text{-}i$<br>‖<br>$CHCO_2C_3H_7\text{-}i$ | None added | $(CH_3O)_2P(S)SCH(CO_2C_3H_7\text{-}i)CH_2CO_2C_3H_7\text{-}i$ (43) | 134 |
| | $CH_3CCO_2C_3H_7\text{-}n$<br>‖<br>$CHCO_2C_3H_7\text{-}n$ | None added | $CH_3CHCO_2C_3H_7\text{-}n$ (10)<br>│<br>$(CH_3O)_2P(S)SCHCO_2C_3H_7\text{-}n$ | 535 |
| | $CH_3CCO_2C_3H_7\text{-}i$<br>‖<br>$CHCO_2C_3H_7\text{-}i$ | None added | $CH_3CHCO_2C_3H_7\text{-}i$ (15)<br>│<br>$(CH_3O)_2P(S)SCHCO_2C_3H_7\text{-}i$ | 535 |
| | $CHCO_2C_4H_9\text{-}i$<br>‖<br>$ClCCO_2C_4H_9\text{-}i$ | None added | $(CH_3O)_2P(S)SCH(CO_2C_4H_9\text{-}i)CH_2CO_2C_4H_9\text{-}i$ (43) | 134 |

| $(C_2H_5O)_2P(S)SH$ | | Conditions | Product | References |
|---|---|---|---|---|
| $CH_3COCO_2C_2H_5$ ‡ | | None added | $CH_3CHCOC_2H_5$ • (22) [ \|CHO ] | 535 |
| $CH_2=CHCN$ | | None added | $(CH_3O)_2P(S)SCH_2CH_2CN$ (33) | 534, 134 |
| $CH_2=CHCHO$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CHO$ (34) | 134 |
| $CH_2=CHCO_2CH_3$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CO_2CH_3$ (83) | 534, 134 |
| $CH_2=CHCO_2C_2H_5$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CO_2C_2H_5$ (71) | 534, 134 |
| | | None added | $(C_2H_5O)_2P(S)SCH_2CH(CH_3)OCOCH_3$ (89) | 534, 134 |
| | | None added | $(C_2H_5O)_2P(S)SCH(CH_3)CH_2CO_2C_2H_5$ (89) | 635 |
| $CHCO_2C_2H_5$ ‡ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CH_3$ (31) [ \|CHCO₂C₂H₅ ] | 134 |
| $CH_2=CHCO_2CH_3$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CO_2CH_3$ (12) | 535 |
| $C_4H_9CH=CH_2$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2C_4H_9$ (84) | 536, 634, 134 |
| $CH_2=CHCH_2Cl$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CH_2Cl$ (16) [ $CH_2CO_2CH_3CH_2Cl$ ] | 535 |
| | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2C_3H_5$ (30) [ \|CHCO₂C₂H₅ ] | 535 |
| $CH_2=CHC_2H_5$ | | None added | $(C_2H_5O)_2P(S)SCH_2CH_2CH_2CO_2C_2H_5$ • $CH_2CO_2C_2H_5$ (89) | 534, 134 |
| $CH_2=CH—CH_2$ ₙ | | Peroxide | $(C_2H_5O)_2P(S)S(SC_2H_5)_n$-ᵃ (76) | 536 |

| Reactant | Additive | Product | Ref. |
|---|---|---|---|
| $CH_3CO_2C_2H_5$ | None added | $CH_3CO_2C_2H_5$, (14) | 535 |
|  |  | $(n\text{-}C_3H_7O)_2P(S)SCHCO_2C_2H_5$ |  |
|  |  | $(n\text{-}C_3H_7O)_2P(S)SCH(OC_2H_5)CH_2CO_2C_2H_5$, + (44) | 134 |
| $CH_3CHCO_2C_2H_5$ <br> $|$ <br> $CH_3CO_2C_2H_5$ | None added | $CH_3CO_2C_2H_5$ | 535 |
| $CH_3CH_2CO_2C_2H_5$ | None added | $CH_3CHCO_2C_2H_5$, n (23) | 134 |
| $CH_3CO_2C_2H_5$ <br> $|$ <br> $CH_3CO_2C_2H_5$ | None added | $(n\text{-}C_3H_7)P(S)SCHCO_2C_2H_5$, + (35) | 134 |
| $CH_3CHCO_2C_2H_5$ <br> $|$ <br> $CH_3CO_2C_2H_5$ | None added | $CH_3CO_2C_2H_5$ | 536 |
| $CH_3CO_2C_2H_5$ <br> $|$ <br> $CH_3CH_2CO_2C_2H_5$ | None added | $CH_3CHCO_2C_2H_5$, n (22) <br> $|$ <br> $(n\text{-}C_3H_7O)_2P(S)SCHCO_2C_2H_5$ | 536 |
|  | None added | $CH_3CHCO_2C_2H_5$, + (13) <br> $|$ <br> $(n\text{-}C_3H_7O)_2P(S)SCHCO_2C_2H_5$ | 536 |
| $(₂C_3H_7O)_2P(S)SH$ | | | |
| $CH_3CO_2C_2H_5$ | None added | $CH_2$=CHCN <br> $(n\text{-}C_4H_9O)_2P(S)SCH_2CH_2CN$ (45) | 134 |
| $CH_2$=CHCN | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2CHO$ | 534, 134 |
| $CH_2$=CHCHO | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2COCH_3$ (60) | 134 |
| $CH_2$=CHCOCH$_3$ | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2CO_2CH_3$ (47) | 534, 534 |
| $CH_2$=CHCO$_2$CH$_3$ <br> $CH_2$=CHC$_4$H$_9$ | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2C_4H_9$ (66) | 537, 534, 134 |
| $CH_3CO_2C_2H_5$ | None added | $CH_2CH_2CO_2C_2H_5$ (39) | 134 |
| $CH_2$=CHC$_4$H$_{11}$, n | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2C_4H_{11}$, n (68) | 537 |
| $CH_2$=CH·CO$_2$C$_4$H$_9$ | None added | $(i\text{-}C_4H_9O)_2P(S)SCH_2CH_2CH_2CO_2C_4H_9$ (17) | 535 |
| $CH_2CO_2C_2H_5$ |  | $CH_2CO_2C_2H_5$ | |

## TABLE X—Continued

### II. Addition of Thiol Phosphoric Acid Derivatives to Olefins—Continued

| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| (i-C$_3$H$_7$O)$_2$P(S)SH (contd.) | CH$_3$CCO$_2$C$_3$H$_7$-n<br>=CHCO$_2$C$_3$H$_7$-n | None added | CH$_3$CHCO$_2$C$_3$H$_7$-n<br>(i-C$_3$H$_7$O)$_2$P(S)SCHCO$_2$C$_3$H$_7$-n (16) | 535 |
| | CH$_3$CCO$_2$C$_4$H$_9$-n<br>=CHCO$_2$C$_4$H$_9$-n | None added | CH$_3$CHCO$_2$C$_4$H$_9$-n<br>(i-C$_3$H$_7$O)$_2$P(S)SCHCO$_2$C$_4$H$_9$-n (23) | 535 |
| (n-C$_4$H$_9$O)$_2$P(S)SH | CH$_2$=CHCN | None added | (n-C$_4$H$_9$O)$_2$P(S)SCH$_2$CH$_2$CN (26) | 534, 134 |
| | CH$_2$=CHCHO | None added | (n-C$_4$H$_9$O)$_2$P(S)SCH$_2$CH$_2$CHO (28) | 134 |
| | CH$_2$=CHCH$_2$OH | None added | 1:1 adduct (14) | 134 |
| | CH$_2$=CHCOCH$_3$ | None added | (n-C$_4$H$_9$O)$_2$P(S)SCH$_2$CH$_2$COCH$_3$ (25) | 134 |
| | CH$_2$=C(CH$_3$)CO$_2$CH$_3$ | None added | (n-C$_4$H$_9$O)$_2$P(S)SCH$_2$CH(CH$_3$)CO$_2$CH$_3$ (38) | 534, 134 |
| | CH$_3$CO$_2$CH$_3$<br>=CHCO$_2$CH$_3$ | None added | CH$_3$CHCO$_2$CH$_3$<br>(n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$CH$_3$ (14) | 535 |
| | C$_2$H$_5$CH=CH$_2$ | None added | (n-C$_4$H$_9$O)$_2$P(S)SCH$_2$CH$_2$C$_4$H$_5$ (94) | 637, 634, 134 |
| | CH$_3$CO$_2$C$_2$H$_5$<br>=CHCO$_2$C$_2$H$_5$ | None added | (n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$C$_2$H$_5$ (40)<br>CH$_2$CO$_2$C$_2$H$_5$ | 534, 134 |
| | CH$_2$=CHC$_6$H$_{13}$-n | None added | (n-C$_4$H$_9$O)$_2$P(S)SC$_6$H$_{13}$-n (91) | 537 |
| | CH$_3$CCO$_2$C$_2$H$_5$<br>=CHCO$_2$C$_2$H$_5$ | None added | CH$_3$CHCO$_2$C$_2$H$_5$<br>(n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$C$_2$H$_5$ | 535 |
| | CH$_3$CCO$_2$C$_3$H$_7$-n<br>=CHCO$_2$C$_3$H$_7$-n | None added | CH$_3$CHCO$_2$C$_3$H$_7$-n<br>(n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$C$_3$H$_7$-n (11) | 535 |
| | CH$_3$CCO$_2$C$_4$H$_9$-n<br>=CHCO$_2$C$_4$H$_9$-n | None added | CH$_3$CHCO$_2$C$_4$H$_9$-n<br>(n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$C$_4$H$_9$-n (11) | 535 |
| | CH$_3$CCO$_2$C$_4$H$_9$-i<br>=CHCO$_2$C$_4$H$_9$-i | None added | CH$_3$CHCO$_2$C$_4$H$_9$-i<br>(n-C$_4$H$_9$O)$_2$P(S)SCHCO$_2$C$_4$H$_9$-i (25) | 535 |

| | | | |
|---|---|---|---|
| (n-C₄H₉O)P(S)SH | CH₂=CHCN | (n-C₄H₉O)P(S)SCH₂CH₂CN (44) | 534, 134 |
| | CH₂=CHCOOCH₃ | (n-C₄H₉O)P(S)SCH₂CH₂CO₂CH₃ (58) | 534, 134 |
| | CH₃—CHOOOCH₃ | (n-C₄H₉O)P(S)SCH(CH₃)CO₂CH₃ (43) | 534, 134 |
| | CH₂=CHCH₂CO₂CH₃ | (n-C₄H₉O)P(S)SCH₂CH(CH₃)CO₂CH₃ (56) | 534, 134 |
| | | | |
| | CH₂CHOOCH₃ | | 535 |
| | CH₂COOCH₃ | | |
| | | | |
| | CH₃CHOOCH₃ | None added | CH₃CHOOCH₃ |
| | CHOO₂CH₃ | | |
| | | | |
| (C₂H₅O)₂P(S)SH | CH₂=CHCN | (C₂H₅O)₂P(S)SCH₂CH₂CN (18) | 534, 134 |
| | CHOO₂CH₃ | None added | (C₂H₅O)₂P(S)SCH₂CH₂CO₂C₂H₅ (15) | 534, 134 |
| | CHOO₂C₂H₅ | | |
| | | | |
| | | CH₂CHOO₂C₂H₅ | 535 |
| | CH₂CHOO₂C₂H₅ | None added | C₄H₉CHOO₂C₂H₅ (32) | 535 |
| | | | |
| (p-ClC₄H₄O)₂P(S)SH | CH₂=CHCN | (p-ClC₄H₄O)₂P(S)SCH₂CH₂CN (53) | 535 |
| | CH₂CHOO₂CH₃ | None added | (p-ClC₄H₄O)₂P(S)SCH₂CH₂CO₂CH₃ (43) | 535 |
| | CH₂=CHCH₂CO₂CH₃ | None added | (p-ClC₄H₄O)₂P(S)SCH₂CH(CH₃)CO₂CH₃ (74) | 535 |
| | | | |
| | | CH₃CO₂C₄H₉ | 535 |
| (C₄H₉O)₂P(S)SH | CH₂=CHCN | (C₄H₉O)₂P(S)SCH₂CH₂CN (45) | 533 |
| | CH₂CHOO₂CH₃ | None added | (C₄H₉O)₂P(S)SCH₂CH₂CO₂CH₃ (47) | 535 |
| | CH₂=CHCH₂CO₂CH₃ | None added | (C₄H₉O)₂P(S)SCH₂CH(CH₃)CO₂CH₃ (72) | 535 |
| | CHOO₂C₄H₉ | None added | | |
| | | | |
| | | CH₃CO₂C₄H₉ | 535 |
| (n-C₄H₉O)₂P(S)SH | CH₂=CHCN | (n-C₄H₉O)₂P(S)SCH₂CH₂CN (79) | 537 |
| | CH₃=CHC₄H₁₀ᵇ | None added | (n-C₄H₉O)₂P(S)SC₄H₁₀ᵇ (57) | 537 |

*Note.*—References 585 to 631 are on pp. 371–376.
ᵇ No structure was given for this product.

## TABLE X—Continued

### I. Addition of Heterocyclic Thiols to Olefins
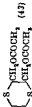
| Thiol | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| (1,3,4‑thiadiazole‑2,5‑dithiol) $\substack{N-N\\HS-S\quad S-SH}$ | $C_6H_5CH{=}CH_2$ | None added | $C_6H_5CH_2CH_2S{-}\!\!\overset{N-N}{\underset{S}{\diagup}}\!\!{-}SH$ (92) | 538 |
| (thienothiophene‑SH) | (maleic anhydride) $\overset{O}{\underset{CO\;\;CO}{\diagup}}$ | None added | [thienothiophene]$SCH(CO_2H)CH_2CO_2H$ (96) | 539 |
| (thienothiophene‑SH) | $C_6H_5CH{=}CH_2$ | None added | [thienothiophene]$SCH_2CH_2C_6H_5$ (67) | 539 |
| (2‑mercaptobenzothiazole) | $CH_2{=}CHSO_2C_6H_4CH_3\text{-}p$ | None added | [benzothiazol‑2‑yl]$SCH_2CH_2SO_2C_6H_4CH_3\text{-}p$ | 447, 506 |

### J. Addition of Aliphatic Thiols to Acetylenes

| Thiol | Acetylene | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $CH_3SH$ | $HC{\equiv}CH + CO$ (890–900 atm.) | Azonitrile | $CH_3SCH{=}CHCHO$ (4)<br>$CH_3SCH_2CH_2SCH_3$ (—) | 540 |
| | $HC{\equiv}CCH_2OH$ | Azonitrile + UV | $CH_3SCH_2CH(SCH_3)CH_2OH$ (65–80) | 184 |
| $HSCH_2CO_2H$ | $HC{\equiv}CC_6H_5$ | None added | $C_6H_5CH{=}CHSCH_2CO_2H$ (42) | 541, 542 |
| $C_2H_5SH$ | $HC{\equiv}CH$ | Peroxide | $C_2H_5SCH_2CH_2SC_2H_5$ (50) | 175 |
| | $HC{\equiv}CCO_2H$ | Peroxide + UV | $C_2H_5SCH{=}CHCO_2H$ (—) | 170 |
| | $HC{\equiv}CCH_2OH$ | Peroxide + UV | $C_2H_5SCH_2CH(CO_2H)SC_2H_5$ (—)<br>$C_2H_5SCH_2CH(CH_2OH)SC_2H_5$ (95) | 170 |
| | $HC{\equiv}COC_2H_5$ | None added | $C_2H_5OCH{=}CHSC_2H_5$ (22–84)<br>(cis and trans) | 106, 543 |
| | $HC{\equiv}CSC_2H_5$ | None added | $C_2H_5OCH(SC_2H_5)CH_2SC_2H_5$ (6–64) | 544 |
| | $CH_3CO_2CH_2C{\equiv}CH$ | Peroxide + UV | $C_2H_5SCH{=}CHSC_2H_5$ (59) | 170 |
| | $CH_3C{\equiv}COC_2H_5$ | Peroxide + azonitrile | $CH_3CO_2CH_2CH(SC_2H_5)CH_2SC_2H_5$ (93) | 545 |
| | $(CH_3)_2C(OH)C{\equiv}CH$ | Peroxide + UV | $C_2H_5SC(CH_3){=}CHOC_2H_5$ (74)<br>$(CH_3)_2C(OH)CH(SC_2H_5)CH_2SC_2H_5$ (72) | 170 |

| | | | |
|---|---|---|---|
| $C_2H_5SCH=CHCH_3$ | | $(CH_3)_2C(OH)CH_2-CH_2SC_2H_5$ (—) | 546 |
| | | and/or | |
| $C_2H_5SCH=CHCH_3$ | None added | $C_2H_5SCH_2-C(CH_3)(SC_2H_5)C_2H_5$ (74) | 170 |
| $HOCH=CHSC_2H_5$ | Peroxide + UV | $C_2H_5SCH=CClCH_2SC_2H_5$, a (93) | 549 |
| $HO_2C-CH=CHSC_2H_5$ | Peroxide + UV | $C_2H_5[SCH_2CH(SC_2H_5)]_nC_2H_5$, a (94) | 447 |
| | Peroxide + UV | $C_2H_5SCH_2-CH(SC_2H_5)C_2H_5$, a (94) | 170 |
| | $MgCl_2$ | $C_2H_5SCH_2-CH_2C_2H_5$, a (—) | 439, 177 |
| $C_2H_5SCH_2-CH_2C_6H_5$ | 2 (and more) | $(C_2H_5)_2CHCH_2SC_2H_5$ (68) | 549 |
| $(C_2H_5)_2C(OH)CH=CH_2$ | Peroxide + UV | $C_2H_5SCH_2-CH(OH)C_2H_5$ (68-90) | 172 |
| $(CH_3)_2C(OH)CH=CH_2$ | Peroxide + UV | $C_2H_5SCH_2-CH(OH)C_6H_5$, a (50) | 544 |
| $C_6H_5CH=CH_2$ | Peroxide + UV | $C_2H_5SCH_2-CH_2C_6H_5$, a (93) | 170 |
| $CH_3CO_2CH_2CH=CH_2$ | Peroxide + UV | $C_2H_5SCH_2CH(SC_2H_5)CH_2CH_2OCOCH_3$ (92) | 170 |
| | | $C_2H_5SCH_2-CH(OH)C_4H_9$, a (98) | 549 |
| | Azonitrile | | 172 |
| | | | |
| $C_2H_5SCH=CHCO_2C_2H_5$ | Peroxide | $C_2H_5SCH_2-CHO_2C_2H_5$ (56) | 172 |
| | | | 550 |
| $HO_2C-CH=CHSC_2H_5$ | Azonitrile | $C_2H_5SCH=CHCH=CHSC_2H_5$ (60) | |
| | | | 549 |
| $HO_2C-CH=CHSC_2H_5$ | Azonitrile |  (90) | |
| | | | |
| $C_6H_{13}CH=CHCO_2C_2H_5$ | Azonitrile |  (82) | 172 |
| $HO_2C-CH=CHCO_2C_2H_5$ | UV + azonitrile | $C_2H_5SCH=CClCH_2CH_2CH_2C_4H_9$ (39) | 549 |
| $C_6H_5CH=CH_2$ | None added | $C_2H_5OCH=CHSC_2H_5$ (75) | 166 |
| | | $C_2H_5OCH(SC_2H_5)CH_2C_6H_5$, a (4) | |

$n$-$C_3H_7SH$

Note: *References 365 to 551 are on pp. 371-376*

TABLE X—Continued

J. Addition of Aliphatic Thiols to Acetylenes—Continued

| Thiol | Acetylene | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| n-C₃H₇SH (contd.) | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₃H₇-n)=CHOC₂H₅ (50) | 172 |
| (CH₃)₂CHSH | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₃H₇-i)=CHOC₂H₅ (89) | 172 |
| n-C₄H₉SH | HC≡CH | Peroxide | n-C₄H₉SCH₂CH₂SC₄H₉-n (93) | 175 |
|  | HC≡CH + CO (2450–2950 atm.) | Peroxide | n-C₄H₉SCH=CHCHO (17) | 175 |
|  | HC≡CCH₂OH | Mercuric acetate + UV | n-C₄H₉SCH₂CH₂SC₄H₉-n (32), n-C₄H₉SCH₂CH(SC₄H₉-n)CH₂OH (50) | 184 |
|  | HC≡CCH=CHCH₃ | Azonitrile | CH₃SCH=CHCH=CHCH₃ (22), CH₃SCH=CHCH=CHC₄H₉-n (33), n-C₄H₉SCH=CHCH=CHSC₄H₉-n (12) | 551 |
|  | HC≡CCH=CHSC₂H₅ | Azonitrile | C₂H₅SCH=CHCH=CHSC₄H₉-n (34), C₄H₅SCH=CHCH=CHSC₄H₉-n (44), n-C₄H₉SCH=CHCH=CHSC₄H₉-n (20) | 551 |
|  | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(OH)(SC₄H₉-n)=CHOC₂H₅ (21) | 172 |
|  | C₆H₅C≡CH + CO (800–900 atm.) | Azonitrile | n-C₄H₉SCH=C(CHO)C₆H₅ (9) | 540 |
|  | HC≡CCH=CHSC₄H₉-n | Azonitrile | n-C₄H₉SCH=CHCH=CHSC₄H₉-n (75) | 551 |
| (CH₃)₂CHCH₂SH | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₄H₉-i)=CHOC₂H₅ (80) | 172 |
| CH₃CH₂CH(CH₃)SH | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₄H₉-s)=CHOC₂H₅ (82) | 172 |
| (CH₃)₃CSH | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₄H₉-t)=CHOC₂H₅ (93) | 172 |
| n-C₅H₁₁SH | (CH₃)₂C(OH)C≡COC₂H₅ | Peroxide | (CH₃)₂C(OH)C(SC₅H₁₁-n)=CHOC₂H₅ (92) | 172 |
| C₆H₁₁SH | HC≡CCO₂H | None added | C₆H₁₁SCH=CHCO₂H (30) (cis und trans), (C₆H₁₁S)₂CHCH₂CO₂H (—), (C₆H₁₁S)₂CHCH₃ (—) | 104 |

| | | |
|---|---|---|
| HC≡CH | None added | [diagram with cyclohexyl groups, trans]  SC(CO₂H)₂=CHCO₂H (46) | 104 |
| HC≡CH + CO | Peroxide | (S₄H₄C(OH)₂=CHCO₂H, 89) | 172 |
| HC≡C(OH)C≡CH(and deriv. addn.) | | | |
| HC≡C·CO₂H | Aromatic | C₅H₅SCH₂SCH(CH₂)₂CH₂C₅H₅ (94) | 175 |
| HC≡CCH₂OH | Atomtria | C₆H₅CH₂SCH₂CH(OH)C₂H₅ (79) | 175 |
| | Peroxide | HC≡CH₂SCH₂CH₂SCH₂C₂H₅ (79) | 165 |
| | Mercapto | C₆H₅CH₂SCH₂CH₂CO₂C₂H₅ (30) | 184 |
| | None added + UV | C₆H₅C(CH₂=CHSCH₂C₇H₅ (74) | 108 |
| | Non added | C₆H₅CH₂SCH₂=CHSCH₂H₅ (46) | 544 |
| | Non added | (CH₂)₄C(OH)C≡SCH₂C₆H₅=CHSCH₃ (76) | 172,543 |
| | Peroxide | (C₂H₄)C(OH)₂CHCH₂=CHSC₂H₅ (33) | 106 |
| | Peroxide | C₆H₅SCH₂=C₆HS₂CH(CP₄)₂Hₙ (81) | 172 |
| | Peroxide | C₆H₅SCH₂=CHSC₆H₅CO₂C₂H₅ (77) | 172 |
| | Non added | (CH₂)₂CO₂H(SC₆H₅, n)=CHₙCHC₄H₅ (87) | 544 |
| | | (C₄H₅)₂SC₂=CHSC₆H₅ (90) | |

C₆H₅CH₂SR

| | | | |
|---|---|---|---|
| HO₂CC≡CCO₂H·H₂O | Peroxide + UV | [diagram] S–CH₂COCH₃ (42)  S–CH₂COCH₃  + polymer | 170 |
| (CH₂)₄C(OH)C≡CCO₂C₂H₅ | | | |

HSCH₂CH₂SH     CH₃CO₂CH₂C≡CCH₂OCOCH₃

*Note:* References 385 to 531 are on pp. 371–376.

TABLE X—Continued

K. Addition of Thiol Acids to Acetylenes

| Thiol | Acetylene | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| CH₃COSH | HC≡CCO₂H | None added | CH₃COSCH=CHCO₂H (—) (cis and trans) + diadduct | 105 |
|  | HC≡CCH₂OH | Azonitrile + UV | CH₃COSCH=CHCH₂OH (10) | 174, 170 |
|  |  | None added | CH₃COSCH₂CH(CH₂OH)SCOCH₃ (03) | 105 |
|  | HO₂CC≡CCO₂H | None added | HO₂CCH(SCOCH₃)CH(CO₂H)SCOCH₃ (07) | 105 |
|  | HC≡CCO₂CH₃ | None added | CH₃COSCH=CHCO₂CH₃ cis (8) trans (18) | 105 |
|  |  | Peroxide | CH₃COSCH₂CH(CO₂CH₃)SCOCH₃ (17) | 552 |
|  | HC≡C(CH₂)₂Cl | Peroxide | CH₃COSCH=CH(CH₂)₂Cl (—) | 171 |
|  | HC≡CCH₂OCH₃ | None added | CH₃COSCH=CHCH₂OCH₃ (15) | 544 |
|  |  | Azonitrile | CH₃COSCH₂CH(SCOCH₃)CH₂OCH₃ (35) | 174 |
|  | HC≡CSC₂H₅ | Peroxide | CH₃COSCH=CHSC₂H₅ (42) | 173 |
|  | HC≡CCH₂OCOCH₃ | None added | CH₃COSCH=CHCH₂OCOCH₃ (10) | 105 |
|  |  | Peroxide | CH₃COSCH₂CH(SCOCH₃)CH₂OCOCH₃ (55) | 173 |
|  | HC≡CCH₂CHOHCH₃ | Peroxide | CH₃COSCH=CHCH₂CHOHCH₃ (30) | 552 |
|  | CH₃O₂CC≡CCO₂CH₃ | Peroxide | CH₃O₂CCH(SCOCH₃)CH(CO₂CH₃)SCOCH₃ (58) | 171, 519 |
|  | HC≡CCHOHCH=CHCH₃ | Peroxide | HC≡CCHOHCH₂CH(OH₂)SCOCH₃ (25); CH₃COSCH₂CH(SCOCH₃)CH(OH)CH=CHCH₃ (11) | 519 |
|  | HC≡CCH₂CH₂OCOCH₃ | None added | CH₃COSCH=CHCH₂CH₂OCOCH₃ (27) |  |
|  | HC≡CC₄H₉-n | None added | CH₃COSCH=CHC₃H₇-n (up to 54); CH₃COSCH₂CH(SCOCH₃)C₄H₉-n (up to 70) | 519 |
|  | HC≡CC(CH₃)₃ | None added | CH₃COSCH=CHC(CH₃)₃ (—) |  |
|  | HC≡CCHOHC₃H₇-n | None added | CH₃COSCH=CHCHOHC₃H₇-n (up to 67); CH₃COSCH₂CH(SCOCH₃)CHOHC₃H₇-n (15) | 173 |
|  | HC≡CC₆H₅ | None added | CH₃COSCH=CHC₆H₅ (85) | 510, 171, 542 |

| | | | |
|---|---|---|---|
| HO₂C(CH₂)₁₀C≡CH | None added | HO₂C(CH₂)₁₀CH=CHSOOCH₃ (26); CH₃COSCH₂CH₂SOOCH₃, CH₃COS(CH₂)₂SO₂CH₃ (38) | 171 |
| (structure) C≡CH | None added | (structure) CH=CHSOOCH₃, (up to 90) | 519 |
| (structure) | | CH₃SOOCH₂CH₂SOOCH₃ (up to 44) | |
| (structure) OH, C≡CH | Peracid | (structure) OH, CH=CHSOOCH₃ (57) + dehydration product | 173 |
| | | | |
| | | (structure) CH₃SOOCH₂CH₂SOOCH₃ (4) | |
| HO₂CCH₂C₁₂H₂₅ | None added | CH₃COSCH=CHC₅H₁₁ (68) | 519 |
| C₆H₁₃C≡C₂H₅ | None added | C₆H₁₃CH₂SOCH₂CH₂CO₂H, CH₃COSOCCH₃ ⋅ (—) | 519 |
| C₆H₅CHOHC≡CH | UV | C₆H₅CHOHC≡CHSOOCH₃, CH₃COSOCH₃ (74) | 173 |
| | | C₆H₅CH₂OHCHCH₂SOOCH₃, CH₃COSOCH₃, CH₃SOCH₃ (11) | |
| p-CH₃OC₆H₄C≡CH | None added | p-CH₃OC₆H₄CH₂CH=CHSOOCH₃ (74) | 171 |
| HO₂C₂H₁CH₂C≡CH | Acetone + | (CF₃COS)₂CH=CHCO₂H (61) | 174 |
| HOC(CH₃)₂C≡CH | UV | HOC(CH₃)₂CH=CH₂SOCH₃ (65) | 553 |
| HC₆CO₂C₄H₄ | None added | C₂H₅CO₂SCH=CHC₄H₄ (—) | 519 |
| HC≡CR₂CH₃ | None added | C₂H₅CO₂SCH=CHC₃H₅ (16–20) | 519 |
| C₂H₅CO₂SC≡CH | None added | C₂H₅CO₂SC=CHC₄H₃ (18) | 544 |
| HO₂CC≡CH | None added | (CH₃)₂C(OH)C≡CH=CHSO₂C₄H₄ (24) | 544 |
| HOC≡C₄H₁₁ | None added | C₂H₅CO₂SCH=CHC₄H₃ (—) | 519 |

*Note.*— Reference 185 to 531 are on pp. 311–316.

‡ The structure was not proved.

4

TABLE X—Continued

### L. Addition of Aromatic Thiols to Acetylenes

| Thiol | Acetylene | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5SH$ | $HC{\equiv}CH + CO$ (920–960 atm.) | Azonitrile | $C_6H_5SCH{=}CHCHO$ (9) | 175 |
|  | $HC{\equiv}CCH_2OH$ | Mercuric acetate + UV | $C_6H_5SCH_2CH_2SC_6H_5$ (63) | 184 |
|  |  | Peroxide | $C_6H_5SCH_2CH(OH)SC_6H_5$ (40) | 172 |
|  | $(CH_3)_2C(OH)C{\equiv}COC_2H_5$ | None added | $(CH_3)_2C(OH)C(SC_6H_5){=}CHOC_2H_5$ (86) | 541 |
|  | $HC{\equiv}CC_6H_5$ | Azonitrile | $C_6H_5SCH{=}CHC_6H_5$ (97) | 550 |
|  | $HC{\equiv}CCH{=}CHSC_6H_5$ | Azonitrile | $C_6H_5SCH{=}CHCH{=}CHSC_6H_5$ (94) | 549 |
|  | [cyclohexene ring] | Azonitrile | [cyclohexene ring] (93) | 549 |
|  | $HC{\equiv}CCH{=}CHOCH_2C_6H_5$ |  | $C_6H_5SCH{=}CHCH{=}CHOCH_2C_6H_5$ (81) | 549 |
| $p\text{-}BrC_6H_4SH$ | $(CH_3)_2C(OH)C{\equiv}COC_2H_5$ | Peroxide | $(CH_3)_2C(OH)C(SC_6H_4Br\text{-}p){=}CHOC_2H_5$ (87) | 172 |
| $p\text{-}ClC_6H_4SH$ | $HC{\equiv}CSC_6H_5$ | None added | $p\text{-}ClC_6H_4SCH{=}CHSC_6H_5$ (59) | 544 |
|  | $(CH_3)_2C(OH)C{\equiv}COC_2H_5$ | Peroxide | $(CH_3)_2C(OH)C(SC_6H_4Cl\text{-}p){=}CHOC_2H_5$ (75) | 172 |
| $p\text{-}CH_3C_6H_4SH$ | $(CH_3)_2C(OH)C{\equiv}COC_2H_5$ | Peroxide | $(CH_3)_2C(OH)C(SC_6H_4CH_3\text{-}p){=}CHOC_2H_5$ (72) | 172 |
|  | $HC{\equiv}CC_6H_5$ | None added | $p\text{-}CH_3C_6H_4SCH{=}CHC_6H_5$ (100) | 554, 541 |
| $p\text{-}CH_3CONHC_6H_4SH$ | $C_2H_5O_2CC{\equiv}CCO_2C_2H_5$ | None added | $p\text{-}CH_3CONHC_6H_4SC(CO_2C_2H_5){=}CHCO_2C_2H_5$ (—) | 555 |
| $p\text{-}t\text{-}C_4H_9C_6H_4SH$ | $(CH_3)_2C(OH)C{\equiv}COC_2H_5$ | Peroxide | $(CH_3)_2C(OH)C(SC_6H_4C_4H_9\text{-}t\text{-}p){=}CHOC_2H_5$ (96) | 172 |

### M. Addition of Hydrogen Sulfide to Olefins and Acetylenes

| Olefin | Moles $H_2S$: Mole Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $CF_2{=}CFCl$ | 1.02 | UV | $CHFClCF_2SH$ (43) <br> $(CHFClCF_2)_2S$ (10) <br> $(CHFClCF_2)_2S_2$ (31) | 198, 199a |
| $CH_2{=}CHCl$ | ~1 | UV | $CH_2ClCH_2SH$ <br> $(CH_2ClCH_2)_2S$ } (70–80) | 556, 191 |
| $CH_2{=}CHSiCl_3$ | 0.5 | None added | $(Cl_3SiCH_2CH_2)_2S$ (50) | 209 |
| $CF_2{=}CF_2$ | 1 | UV | $CHF_2CF_2SH$ (—) <br> $(CHF_2CF_2)_2S$ (—) <br> $(CHF_2CF_2)_2S_2$ (—) | 198, 199a |

| Olefin | | Conditions | Products | Reference |
|---|---|---|---|---|
| CH₂=CH₂ | | None added | C₂H₅SH (14)  (C₂H₅)₂S (47) | 189 |
| | | Azonitrile | n-C₄H₉SH (1) | 81 |
| CH₂=CH₂ + CO | 1 2 | None added | (C₂H₅)₂S (16) | 557 |
| CH₃·CHN₂] | | UV | (C₃H₇)₂S (CH₃SC₂H₄)₂ (18) | 101,558, 559,560, 458,201 |
| CH₃CH=CH₂ | | | n-C₄H₉SH (63) | 190 |
| | | Azonitrile | (n-C₇H₁₅)₂S (33) | 190 |
| HOCH₂CH=CH₂ | 2 5 | Azonitrile | (HOCH₂)₃SiH (39)  [HO(CH₂)₃]₃S (39) | 190 |
| CH₂=CHCH₂NH₂ | 2 2 | UV | NH₂(CH₂)₃SH (22)  [NH₂(CH₂)₃]₂S (34) | 202 |
| (CH₂=CH)₂O | 8 5 | Azonitrile | Polymer? (95)  (mol wt = 1000–1600) | 135 |
| | | | HSCH₂CH(CH₃)CH₂C₄H₉SH (47)  HSCH₂OCH₂SCH₂OCH₂CH₂SH (27)  HS(C₂H₄O)₄C₂H₄S[C₂H₄SC₂H₄]₆SH (17) | 191,556 191,658 |
| CH₂CH=CClCH₃ | 4 4 | Peroxide (H₂O₂) | HS[Si(CH₃)₂O]Si(CH₃)₂SiH (47)  n-C₄H₉SH (13) | 201 |
| C₂H₅CH=CH₂ | | | CH₃CH(SH)C₂H₅ (17)  (CH₃CHClCH₃)₂S (62) | |
| (CH₃)₂C=CH₂ | 4 5 | O₃ | [C₂H₅CH(CH₃)]₂S (6)  (CH₃)₂CHCH₂SH (30) | 197 |
| C₂H₅OCH=CH₂ | 1 4 | O₃ | C₂H₅OCH₂CH₂SH (26)  C₂H₅OCH(CH₃)CH₂OC₂H₅ (2) | 179 |
| C₄H₉SCH=CH₂ | 1 5 | UV | C₄H₉SCH₂CH₂SH (39)  (C₄H₉SCH₂CH₂)₂S (40) | 561 |



SH cyclopentene: trans (113)  cis (51)

*Note: References 385 to 631 are on pp 271–278.  ʃ No structure was given for this product.*

## TABLE X—Continued

### M. Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued

| Olefin | Moles H₂S: Mole Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| n-C₃H₇OCH=CH₂ | 1.2 | None added | n-C₃H₇OCH₂CH₂SH (61)<br>n-C₃H₇O(CH₂)₂S(CH₂)₂OC₃H₇-n (28)<br>n-C₃H₇OCH(CH₃)S(CH₂)₂OC₃H₇-n (5) | 197 |
| (CH₃)₂CHOCH=CH₂ | 1 | None added | (CH₃)₂CHOCH₂CH₂SH (59)<br>(CH₃)₂CHO(CH₂)₂S(CH₂)₂OCH(CH₃)₂ (25)<br>(CH₃)₂CHOCH(CH₃)S(CH₂)₂OCH(CH₃)₂ (10) | 197 |
| (CH₃)₃SiCH=CH₂ | | UV | (CH₃)₃Si(CH₂)₂SH (68)<br>[(CH₃)₃Si(CH₂)₂]₂S (8) | 209 |
| (chlorocyclohexene) | 90 | UV | Cl, SH (62) (cis and trans)<br>Cl Cl S (cyclohexyl) (22) | 97 |
| (N-vinylpyrrolidone) | | Azonitrile | N(CH₂)₂SH (0–10)<br>[ ]₂ S (64–87) | 562 |
| (cyclohexene) | | UV | SH (28)<br>Liquid polymer (Av. mol. wt. = 210) | 191 |
| CH₂=CHCH₂CH₂CH=CH₂ | | Azonitrile or peroxide | (cyclohexyl)₂S (40) | 190, 201 |

| | | | |
|---|---|---|---|
| $(CH_3)_2CHCH_2CH_2O$ | | UV | $+RCH_2OCH(CH_3)_2$ (92) (Av. mol. wt. = 274) 205, 505, 202, 191 |
| 1 | | | |
| $n$ $C_7H_{15}CH=CH_2$ | | Peroxide or UV + $Di(C_7H_{15}-CH_2)_4N$ $n$ $C_7H_{15}CH_2N(CH_2)_2R$ (32) | 204, 436, 554 |
| 8 65 | | Acetonitrile | $(a$ $C_7H_{15}N$ (24) 190 |
| $(CH_3)_2C=C(CH_3)_2$ | | Peroxide or acetonide | $(CH_3)_2CHC(CH_3)_2N$ (35) I 196, 200 |
| 2 0 | | | |
| $n$ $C_5H_{11}OCH=CH_2$ | | None added | $C_5H_{11}OCH_2CH_2N$ (24) 197 |
| 1.4 | | | |

| $(CH_3)_2CHCH_2CH=CH_2$ | | UV | $[(CH_3)_2N(CH_2)_5]_2N$ (26) 209 |
| 3 9 | | | (10) |

| | UV | $[(CH_3)_3N(CH_2)_3]_2N$ (26) 192 |



| $[CH_3CO_2CH_2CH(Cl)-CH_2$ $(CH_3)_2CHCH_2CH_2OCH=CH_2]$ | | Acetonitrile None added | $(CH_3CO_2CH_2CHCICH_2)_2N-H$ (47) 600, 197 |
| 1.3 | | | |
| $C_5H_{11}CH=CH_2$ | | Acetonitrile or $\gamma$-rays | 190, 204, 200 |
| 5 | | | |
| $C_5H_{11}OCH=CH_2$ | | Acetonitrile | 190 |
| 2 1 | | | |
| $C_4H_9CH=CH_2$ | | Azonitrile | 100 |
| 7.3 | | | |

| | | Azonitrile | Monothiol $(C_7H_{14}N)_2f$ (46) Dithiol $(C_7H_{14}N_2)$ (12) 100 |
| 1 | | | |

Note: Footnotes 286 to 631 are on pp. 371-376
f No structure was given for this product.

TABLE X—*Continued*

M. *Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued*

| Olefin | Moles H₂S: Mole Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| (piperidinone, NCH=CH₂) | 4.0 | Azonitrile | NCH₂CH₂SH (3–43); (piperidinone NCH₂CH₂)₂S (39–88) | 562 |
| (CH₃)₂C=CHCH=C(CH₃)₂ | 1.2 | Peroxide + Iron | (CH₃)₂C=CHCH(SH)CH(CH₃)₂ (18); (CH₃)₂CHCH(SH)CH(SH)CH(CH₃)₂ (15) | 193 |
| cyclohexyl-OCH=CH₂ | | Azonitrile | OCH₂CH₂SH (29); (OCH₂CH₂)₂S (68) | 200, 197 |
| [CH₂=C(CH₃)CH₂]₂O | 1 | UV | Polymer (83) (Av. mol. wt. = 661) | 202, 205 |
| (CH₂=CHOCH₂CH₂)₂O | | γ-Rays | (HSCH₂CH₂OCH₂CH₂)₂O (70) | 204 |
| n-C₆H₁₃CH=CH₂ | 2.8 | γ-Rays | n-C₈H₁₇SH (88) | 204 |
|  | 2.0 | Azonitrile | n-C₈H₁₇SH (73) | 190 |
| n-C₅H₁₁CH=CHCH₃ | | Azonitrile | (n-C₈H₁₇)₂S (24); C₈H₁₇SH (66) | 190 |
| (C₂H₅O)₃SiCH=CH₂ | | UV | (C₈H₁₇)₂S (15); (C₂H₅O)₃SiCH₂CH₂SH (5); [(C₂H₅O)₃SiCH₂CH₂]₂S (50) | 200 |
| C₆H₅C(CH₃)=CH₂ | 0.7 | Peroxide (H₂O) | C₆H₅CH(CH₃)CH₂SH (29); [C₆H₅CH(CH₃)CH₂]₂S (2) | 201 |
| cyclohexene-CO₂CH₃, CO₂CH₃ | 6 | Azonitrile | HS-cyclohexane CO₂CH₃, CO₂CH₃ (52) | 190 |

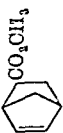| | | | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|---|
| $(CH_3)_2C=CHCH_2)_2$- $C(CH_3)_2$—$CHCH_3$ | 1 13 | $(CH_3)_2CHCH(SH)CH_2)_2CH(CH_3)_2CH_2CH(CH_3)_2$—$CHCH_3$ $(CH_3)_2$—$CH_2$—$CH(CH_3)_2CH_2CH(CH_3)_2CH_2CH_3$,SH (52) | Acetone + UV | | 194 |
| | | $C_7H_{16}S_2$ (5) $(CH_3)_2CHCH(SH)(CH_2)_2CH(CH_3)_2CH_2CH(CH_3)_2$,SH (2) | None added | | 191 |
| $n$-$C_6H_{13}OCH=CH_2$ | 2 95 | ($n$-$C_6H_{13}OCH_2CH_2$)$_2$SH (16) ($n$-$C_6H_{13}OCH_2CH_2$)$_2$S (31) | Azonitrile | | 250 |
| $p$-$(CH_3)_2C_6H_4OCH=CH_2$ | 2 1 | $p$-$(CH_3)_2C_6H_4OCH_2CH_2$SH (36) [$p$-$(CH_3)_2C_6H_4OCH_2CH_2CH_2$]$_2$S (34) | Peroxide (H$_2$O) | | 251 |
| $n$-$C_7H_{14}CH=CH_2$ | | ($n$-$C_7H_{15}$)$_2$S (16) HSCH$_2$CH(CO$_2$C$_2$H$_5$ $n$)(CH$_2$)$_4$ + CH(CO$_2$C$_2$H$_5$)(CH$_2$)$_4$ (—) [$n$-$C_4H_9OCOCH(CH_2)_4$- CH(CO$_2$C$_4$H$_9$ $n$)(CH$_2$)$_4$S$_2$ (—) | Peroxide | | 206 |
| $CH_2=COC_2H_5C_6H_5$ $n$](CH$_3$)$_4$ CH(CO$_2$C$_4$H$_9$ $n$)$_4$ | | | | | |
| $n$-$C_6H_{14}CH=CH_2$ | 7.3 | $n$-$C_6H_{13}CO_2C_2H_5$ $n$](CH$_3$)$_4$ ($a$, $C_7H_{14}$S)SH (72) ($a$, $C_7H_{14}$)$_2$S (18) | Azonitrile | | 190, 177 365, 438 |
| $CH_3(CH_2)_{10}$- $CH=CH(CH_2)_{10}$CO$_2$H | 9 5 | $CH_3(CH_2)_{10}CH(SH)(CH_2)_{10}CO_2H$ (77) | Azonitrile | | 190 |
| $CH_3(CH_2)_{10}CH=CH(CH_2)_{10}$- CO$_2$CH(CH$_3$)$_2$ | | $n$-$C_6H_{13}$·SH (69) $n$-$C_8H_{17}S_2$ (23) $CH_3(CH_2)_{10}CH(SH)(CH_2)_{10}CO_2CH(CH_3)_2$ (73) | Azonitrile | | 190 |
| Acetylene | Mole:H$_2$S:Mole Acetylene | | Catalyst | Products (%) | Refs. |
| $CF_3C≡CH$ | 3 5 | | X ray | $CF_3CH=CHSH$ (73) (cis and trans) $CF_3CH_2CH_2SH$ (20) ($CF_3CH=CH_2$)$_2$SH (9) | 205a |

*Note.* Reference 365 to 441 are on pp. 371–376.

$f$ No structure was given for this product.

## TABLE X—Continued

### M. Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued

| Acetylene | Moles H₂S: Mole Acetylene | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $CH_3C \equiv CH$ | 2 | X-ray | $CH_3CH=CHSH$ (32) (cis and trans) $CH_3CHSHCH_2SH$ (35) Polymer (33) | 208a |
| $CF_3C \equiv CCF_3$ | 3.3 | X-ray | $CF_3CH=C(SH)CF_3$ (60) | 208a |
| $CH_3C \equiv CCH_3$ | 1.8 | X-ray | $CH_3CH=C(SH)CH_3$ (24) (cis and trans) $CH_3CHSHCHSHCH_3$ (41) Polymer (35) | 208a |
| $C_6H_5C \equiv CH$ | 3.3 | X-ray | $C_6H_5CH=CHSH$ (8) $(C_6H_5CH=CH)_2S$ (47) Polymer (45) | 208a |
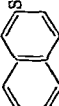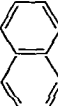
### N. Addition of Bisulfite to Olefins and Acetylenes

| Olefin | Bisulfite | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $CF_3=CF_2$ | $NaHSO_3$ | None or peroxide | $CHF_2CF_2SO_3Na$ (—) | 566 |
| $CF_3=CH_2$ | $NaHSO_3$ | None added | $CHF_2CH_2SO_3Na'$ (—) | 566 |
| $CH_2=CHCl$ | $NaHSO_3$ | $O_2$ | $CH_2ClCH_2SO_3Na$ (90) | 567 |
| $CH_2=CH_2$ (35–40 p.s.i.) | $NH_4HSO_3$ | $O_2$ | $CH_3CH_2SO_3NH_4$ (12) | 210, 217 |
| $CH_2=CH_2$ (700–1000 atm.) | $NaHSO_3$ | Peroxide | $H(CH_2CH_2)_nSO_3Na$ (—) $n = 4$ (average) | 218 |
| $CF_3ClF=CF_2$ | $NaHSO_3$ | Peroxide | $CF_3ClHFCF_2SO_3Na$ (64) | 215 |
| $CH_3CH=CH_2$ | $NH_4HSO_3$ | $O_2$ or $NaNO_2$ + $NaNO_3$ | $CH_3CH_2CH_2SO_3NH_4$ (55) | 210 |
| $HOCH_2CH=CH_2$ | $(Na)KHSO_3$ (pH = 7) | Air | $HO(CH_2)_3SO_3K(Na)$ (94–100) | 221, 220, 568, 569, 570, 210 |
| | $KHSO_3$ (pH = 4) | Air | $KO_3SCH_2CH(SO_3K)CH_2OH$ (—) | 219 |
| $(CH_3)_2C=CH_2$ | $NaHSO_3$ | $O_2$ | $(CH_3)_2CHCH_2SO_3Na$ (62) | 210 |

| | | | | |
|---|---|---|---|---|
| HOCH(CH₂)₂CH₃ | NaHSO₄ | O₂ | HO(CH₂)₄SO₃Na (almost quant.) | 215 |
| | NaHSO₄ | Peroxide | CH₃(CHSO₃Na)₂CH₂OH (—) | 216 |
| n-C₂H₇CF·CF₃ | NaHSO₄ | O₂ | n-C₃H₇CHFCF₂SO₃Na (79) | 215 |
| C₆H₅· | NH₄HSO₄ | None added | C₆H₅SO₃NH₄ (68) | 217 |
| | | | | |
| | NH₄HSO₄ | None added | ⬡SO₂NH₃ (57) | 217 |
| | | | | |
| n-C₃H₅·CH=CH—CH₃ | NaHSO₄ | Peroxide | n-C₃H₇CHFCF₂SO₃Na (73) | 215 |
| C₄H₉CH=CHCH₂OH | NaHSO₄ | O₂ | C₄H₉CH(SO₃NH₄)SO₃NH₄ (30) | 234 |
| p-CH₃C₆H₄SO₂CH=CH₂ | NH₄HSO₄ | O₂ | C₄H₉CH(OH)CH₂SO₃NH₄ (50) | 214, 210, |
| | NaHSO₄ | None added | C₄H₉CH=CHSO₃NH₄ (14) | 571 |
| | | | C₄H₉CH(SO₃NH₄)CH₂ (14) | |
| | | | C₄H₉CH(OH)CH₂SO₃Na (16) | |
| | NaHSO₃ | NaNO₂ | n-C₃H₇CH(SO₃Na)₂ (—) | 214 |
| | | | 11 isomers? (90) | |
| | | | p-CH₃C₆H₄SO₂CH₂CH₂SO₃Na (—) | |
| | NH₄HSO₃ | Peroxide | p-CH₃C₆H₄S(O)OCH₂CH₂SO₂Na (—) | 572, 527 |
| | NaHSO₃ | O₂ | p-CH₃C₆H₄SO₂CH₂CH₂SO₃Na (—) | 210, 573 |
| | NaHSO₃ | None added | | 447, 674, |
| | | | | 225 |
| ⬡SO₂CH=CH₂ | NaHSO₃ | None added | ⬡SO₂CH₂CH₂SO₃Na | 574, 225 |
| | | | | 447 |
| | | | | |
| | | | | |
| (cyclohexene with CH₃) | NH₄HSO₄ | None added | Product not characterized | 447 |
| Fuoss | | | | |
| | | | | |
| CH₂=CH—CH₃ | NH₄HSO₄ | None added | C₇H₁₄NO₂S f (—) | 217 |
| (±) | | | | |

*Note:* References 385 to 631 are on pp. 371–376.

*f* No structure was given for that product.
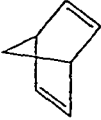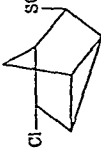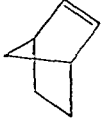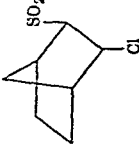
## TABLE X—Continued

### N. Addition of Bisulfite to Olefins and Acetylenes—Continued
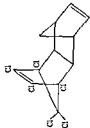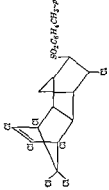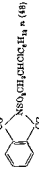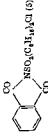
| Olefin | Bisulfite | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $(CH_3)_2C=CH(CH_2)_2\cdot C(CH_3)=CHCH_2OH$ (Geraniol) | $NaHSO_3$ | None added | $C_{10}H_{30}S_2O_7Na_2'$ (—) | 573 |
| $n\text{-}C_8H_{17}CH=CH_2$ | $NH_4HSO_3$ | Peroxide | $n\text{-}C_{10}H_{21}SO_3NH_4$ (77) | 572, 227 |
| $(CH_3)_2C=CH(CH_2)_2\cdot CH(CH_3)CH_2CH_2OH$ | $NaHSO_3$ | None added | $(CH_3)_2CHCH(SO_3Na)(CH_2)_2\cdot CH(CH_3)CH_2CH_2OH$ | 573 |
| [naphthalene]—$SO_2CH_2CH=CH_2$ | $NaHSO_3$ | None added | [naphthalene]—$SO_2CH_2CH_2SO_3Na$ (—) | 447 |
| $n\text{-}C_{10}H_{21}CH=CH_2$ | $NH_4HSO_3$ | Peroxide | $n\text{-}C_{12}H_{25}SO_3NH_4$ (73) | 227, 572 |
| $n\text{-}C_{12}H_{25}CH=CH_2$ | $NH_4HSO_3$ | Peroxide | $n\text{-}C_{14}H_{29}SO_3NH_4$ (90) | 227, 572 |
| $n\text{-}C_{12}H_{25}S(O)CH=CH_2$ | $NaHSO_3$ | None added | $n\text{-}C_{12}H_{25}S(O)CH_2CH_2SO_3Na$ (—) | 447 |
| $n\text{-}C_{12}H_{25}SO_2CH=CH_2$ | $NaHSO_3$ | None added | $n\text{-}C_{12}H_{25}SO_2CH_2CH_2SO_3Na$ (—) | 447, 226 |
| $n\text{-}C_{14}H_{29}CH=CH_2$ | $NH_4HSO_3$ | Peroxide | $n\text{-}C_{16}H_{33}SO_3NH_4$ (22) | 227, 572 |
| $n\text{-}C_{16}H_{33}SCH=CH_2$ | $NaHSO_3$ | None added | $n\text{-}C_{16}H_{33}SCH_2CH_2SO_3Na$ (—) | 447, 574 |
| $n\text{-}C_{18}H_{37}S(O)CH=CH_2$ | $NaHSO_3$ | None added | $n\text{-}C_{18}H_{37}S(O)CH_2CH_2SO_3Na$ (—) | 225, 574 |
| $n\text{-}C_{18}H_{37}SO_2CH=CH_2$ | $NaHSO_3$ | None added | $n\text{-}C_{18}H_{37}SO_2CH_2CH_2SO_3Na$ (—) | 447, 226 |

| Acetylene | Bisulfite | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $HC\equiv CCH_2OH$ | $KHSO_3$ | $O_2$ | $KO_3SCH=C(SO_2K)CH_2OH$ (—) | 210, 575 |
| $HOCH_2C\equiv CCH_2OH$ | $NaHSO_3$ | None added | $HOCH_2CH(SO_3Na)CH(SO_3Na)CH_2OH$ (—) | 224, 575 |
| $n\text{-}C_4H_9C\equiv CH$ | $NaHSO_3$ | $O_2$ | $n\text{-}C_4H_9CH=CHSO_3Na$ (17); $n\text{-}C_4H_9CH(SO_3Na)CH_2SO_3Na$ (32) | 224 |
| $C_6H_5C\equiv CH$ | $NaHSO_3$ | $O_2$ | $C_6H_5CH=CHSO_3Na$ (15); $C_6H_5CH(SO_3Na)CH_2SO_3Na$ (40) | 224 |
| $n\text{-}C_4H_9NHCH(CH_3)C\equiv CH$ | $NaHSO_3$ | None added | $n\text{-}C_4H_9NHCH(CH_3)CH(SO_3Na)CH_2SO_3Na$ (—) | 575 |

### O. Addition of Sulfuryl and Sulfonyl Halides to Olefins

| Halide | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $SO_2Cl_2$ | $CH_2=CH_2$ | Peroxide | $Cl(CH_2CH_2)_nSO_2Cl$ | 238 |
|  | $n\text{-}C_4H_9CH=CH_2 + SO_2$ | Peroxide | $n\text{-}C_4H_9CHClCH_2Cl$ (70); $(n\text{-}C_4H_9CHClCH_2)_2SO_2$ (13) | 230 |

| | | | | |
|---|---|---|---|---|
| CH₃SO₂F | n-C₄H₉CH=CH₂ + SO₂ | Peroxide | n-C₄H₉CH·CHClCH₂Cl (49) | 236 |
| | n-C₆H₁₃CH=CH₂ + SO₂ | Peroxide | (n-C₄H₁₃CHClCH₂)₂SO₂ (21) | 229 |
| | n-C₈H₁₇CH=CH₂ + SO₂ | Peroxide | n-C₄H₉CH·CHClCH₂Cl (61) | 235 |
| | | Peroxide | (n-C₄H₁₃CHClCH₂)₂SO₂ (28) | 235 |
| | CFCl=CF₂ | Peroxide | (n-C₄H₁₇CHClCH₂)₂SO₂ (15) | 235 |
| | | Peroxide | Cl(CF₂CF₂)ₙSO₂F (—) | 235 |
| | CF₂=CF₂ | Peroxide | (n, average = 18) | 234 |
| | | Peroxide | D[(CF₂CF₂)ₙSO₂F]² (—) | 234 |
| | | Peroxide | (n, average = 4–5) | 234 |
| | CH₂=CF₂ | Peroxide | Cl(CF₂CH₂)ₙSO₂F (—) | 234 |
| | | Peroxide | (n, average = 4) | 234 |
| | CH₂=CH₂ | Peroxide | Cl(CH₂CH₂)ₙSO₂F (66) | 234 |
| | | Peroxide | ClCH(CH₃)CH₂SO₂F (16) | 234 |
| | CHCl₂CH=CH₂ | Peroxide | CCl₃CH₂CH(CH₃)SO₂F (45) | 234 |
| | | Peroxide | ClCH₂CH(CH₂SO₂F)₂ (17) | 234 |
| | CH₂=CH₂ | Peroxide | Cl₂CHCH₂CH₂(CH₂)ₙSO₂F (80) | 234 |
| | C₄H₉CH=CH₂ | Peroxide | (CH₃)₂CCH₂CH₂SO₂F (72) | 234 |
| | (CH₂)₄CH=CH₂ | UV | O(CH₂CH₂CH₂SO₂F)₂ (—) | 228 |
| | n-C₆H₁₃CH=CH₂ | UV | n-C₄H₉CHClCH₂SO₂F (73) | 229 |
| | CH₃CH=CClCH₂COOH | Peroxide | n-C₄H₉CHClCH₂COOH (94) | 228 |
| C₆H₅SO₂Br | CH₃CH₂CH=CH₂ | UV | F₈O₄CH₂CH₂(CH₂)ₙSO₂F (72) | 228 |
| | C₆H₅CH=CH₂ | UV | n-C₄H₉CH(SO₂C₆H₅)CH₂Br (99) | 228 |
| | CH₃CH=CHCH₃ | UV | C₆H₅SO₂CH₂CHBr·CH₃ (—) | 228 |
| | CH₃CH=CHCH₃ | Peroxide | C₆H₅SO₂CH(CH₃)CHBrCH₃ (106) | 228 |
| | C₆H₅CH=CH₂ | Peroxide | C₆H₅SO₂CH₂CHBr·C₆H₅ (80) | 228 |

(see)

*Note:* References 385 to 631 are on pp. 371–376.
ᶠ No structure was given for this product.

TABLE X—Continued

O. Addition of Sulfuryl and Sulfonyl Halides to Olefins—Continued

| Halide | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| C$_6$H$_5$SO$_2$Br (contd.) | CH$_3$CO$_2$CH$_2$CH=CH$_2$ | Peroxide | C$_6$H$_5$SO$_2$CH$_2$CHBrCH$_2$OCOCH$_3$ (63) | 228 |
| | CH$_2$=C(CH$_3$)CO$_2$CH$_3$ | UV | C$_6$H$_5$SO$_2$CH$_2$CBr(CH$_3$)CO$_2$CH$_3$ (44) | 228 |
| | CH$_2$=CHCH(OCOCH$_3$)$_2$ | UV | C$_6$H$_5$SO$_2$CH$_2$CHBrCH(OCOCH$_3$)$_2$ (90) | 228 |
| | C$_6$H$_5$CH=CH$_2$ | UV | C$_6$H$_5$SO$_2$CH$_2$CHBrC$_6$H$_5$ (90) | 228 |
| p-ClC$_6$H$_4$SO$_2$Cl | CH$_2$=CH$_2$ | Azonitrile | p-ClC$_6$H$_4$SO$_2$CH$_2$CH$_2$Cl (21); p-ClC$_6$H$_4$SO$_2$(CH$_2$)$_4$Cl (32) | 229 |
| | CH$_2$=C(CH$_3$)$_2$ | Peroxide | p-ClC$_6$H$_4$SO$_2$CH$_2$CCl(CH$_3$)$_2$ (75) | 229 |
| | CH$_3$CO$_2$CH$_2$CH=CH$_2$ | Peroxide | p-ClC$_6$H$_4$SO$_2$CH$_2$CHClCH$_2$OCOCH$_3$ (20); p-ClC$_6$H$_4$SO$_2$CH$_2$CH(CH$_2$OCOCH$_3$)CH$_2$CHClCH$_2$OCOCH$_3$ (—) | 241 |
| C$_6$H$_5$SO$_2$Cl | CH$_3$CH=CHCH$_3$ | Peroxide | C$_6$H$_5$SO$_2$CH(CH$_3$)CHClCH$_3$ (80) | 228 |
| | CH$_2$=C(CH$_3$)$_2$ | Peroxide | C$_6$H$_5$SO$_2$CH$_2$CCl(CH$_3$)$_2$ (98) | 228 |
| | CH$_2$=CHC$_6$H$_{13}$-n | Peroxide | C$_6$H$_5$SO$_2$CH$_2$CHClC$_6$H$_{13}$-n (92) | 228 |
| p-CH$_3$C$_6$H$_4$SO$_2$Cl | (cyclohexene) | Peroxide | (cyclohexyl structure) SO$_2$C$_6$H$_4$CH$_3$-p (36) | 140 |
| | (bicyclic diene) | Peroxide or UV | (bicyclic structure, Cl) SO$_2$C$_6$H$_4$CH$_3$-p (47–63) | 140, 232 |
| | (bicyclic diene) | Peroxide or UV | (bicyclic structure, Cl) SO$_2$C$_6$H$_4$CH$_3$-p (64–92) | 140, 232 |

| | | | |
|---|---|---|---|
|  | Peroxide | (9) | 149, 232 |
| CH₂=CHCN | | $C_6H_5SO_2CH_2CH_2OH$ (78) | 228 |
| CH₂=CHCH₂OH | UV | $C_6H_5SO_2CH_2CH_2CN$ (98) | 228 |
| CH₃CH=CHCH₃ (cis or trans) | UV | $C_6H_5SO_2CH_2CH_2CHClCH_3$ (99) | 228, 231 |
| CH₂=CHCOC₂H₅ | UV | $C_6H_5SO_2CH_2CHCOC_2H_5$ (52) | 228 |
| C₆H₅CH=CH₂ | UV |  | 228 |
| C₄H₉CH=CH₂ | UV | $C_6H_5SO_2CH_2CHClC_4H_9$ (73) | 228 |
| CH₂=CHC₅H₁₁-n | Peroxide |  | 240 |

$C_4H_9SO_2I$



Note. References 385 to 651 are on pp. 371–376.

TABLE X—*Continued*

*O. Addition of Sulfuryl and Sulfonyl Halides to Olefins—Continued*

| Halide | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
|  NSO₂Cl (*contd.*) | CH₂=CHC₆H₁₇-*n* | Peroxide |  NSO₂CH₂CHClC₈H₁₇-*n* (64)  <br>  NSO₂(C₁₀H₂₀)₂Cl (9) | 240 |

*P. Miscellaneous Additions to Form Carbon-Sulfur Bonds*

| Addendum | Unsaturate | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| *Unsaturated Thiols* | | | | |
| CH₂=CHCH₂SH | | None added | (C₃H₆S)ₓ (—) | 117, 116 |
| CH₃CH=CHCH₂SH | | None added | Polymer* (—) | 115 |
| CH₂=CH(CH₂)₂SH | | None added | Polymer* (—) | 115 |
| CH₂SH | | None added | (C₅H₆OS)ₓ (—) | 570 |
|  | | None added | Polymer* (—) | 115 |
| CH₂=CH(CH₂)₃SH | | None added | Polymer* (—) | 115 |
| (CH₃)₂C=CHCH₂SH | | None added | Polymer* (80) | 115 |
| CH₂CH₂SH | | (NH₄)₂S₂O₈ + CuSO₄ | Polymer (93) | 118 |
| C₆H₅CH=CHCH₂SH | | None added | (C₉H₁₀S)ₓ (—) | 117 |

| Sulfonyl Halide | Olefin | Conditions | Product | Reference |
|---|---|---|---|---|
| CF₃SO₂Cl | CRCH=CF₂ | UV | CF₃SO₂CF₂Cl (142) | 245 |
| | | | CF₃SO₂CF₂CF₂Cl (5) | 245 |
| | CHF=CF₂ | UV | CF₃SO₂CHFCl (160) | 245 |
| | | | CF₃SO₂CHFCF₂Cl (111) | 245 |
| | CH₂=CF₂ | UV | CF₃SO₂CF₂CH₂Cl (140) | 245 |
| | | | CF₃SO₂CH₂CF₂Cl (111) | 245 |
| | | | CF₃SO₂CH₂CF₂CH₂Cl (73) | 245 |
| | CF₂=CFCF₃ | UV | CF₃SO₂CF₂CHCl₂ (4) | 245 |
| | | | CF₃SO₂CF₂CFClCF₃ (108) | 245 |
| | | | CF₃SO₂CF(CF₃)CF₂SCF₃ (110) | 245 |
| | | | ClCₙF₂ₙCl (20) | 245 |
| | | | CF₃SO₂CF₂SCF₃ — | 245 |
| | | | 1,1 adduct (59) | 245 |
| | CH₂=ClCF=CF₂ | UV | CH₂OClCF₂CF₂CF₂Cl (16) | 245 |
| | | | CH₂Cl OClCF₂SCF₃ (24) | 245 |
| | | | CH₂ClOClCF₂CFClCl (11) | 245 |
| | | | CH₂OClCF₂CF₂SCF₃ (11) | 245 |
| | | | CF₃SCF₂— | 245 |
| | | | 1,1 adduct (59) | 245 |
| Cl₃CSCl | CH₂=ClCH(Cl)Cl | UV or peroxide | (structure) SClₙCl₃ (50) | 243 |
| | | | 1,1 adduct (95) | 244 |
| | CH₃CH₂CH₂CH₂=CH₂ | UV or peroxide | (structure with Cl) SClₙCl₃ (68) | 243 |
| | | | 1,1 adduct (89) | 243, 244 |
| | CH₂=ClC₆H₅ | UV or peroxide | (benzofuran structure) * | 243, 244 |
| | | | 1,1 adduct (21) | 244 |

ᵃ See references 245 to 251 are on pp. 311-316.
ᵇ No structure was given for this product.
ᶜ The polymer was not characterized.

## TABLE X—Continued

### P. Miscellaneous Additions to Form Carbon-Sulfur Bonds—Continued

| Addendum | Unsaturate | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| *Sulfonyl Halides (contd.)* | | | | |
| Cl₃CSCl | $C_6H_5CH=CH_2$ | UV or peroxide | $C_6H_5CH(SCCl_3)CH_2Cl$ (54) | 243, 244 |
| | $CH_2=CHC_6H_{13}$-n | UV | 1:1 adduct^j (66) | 243 |
| | (indene structure) | Peroxide | 1:1 adduct^j (17) | 244 |
| $C_6H_5SCl$ | (cyclopentene-CO₂CH₃ structure) | Peroxide | $C_6H_5S$—(ring)—$CO_2CH_3$ (5) | 577 |
| | | | $(C_6H_5)_2S_2$ (—) | |
| *Sulfur Chloride Pentafluoride* | | | | |
| $SF_5Cl$ | $CF_2=CF_2$ | Peroxide + UV | $SF_5CF_2CF_2Cl$ (24) $SF_5(CF_2CF_2)_2Cl$ (—) $SF_5(CF_2CF_2)_3Cl$ (—) | 249 |
| | $CFCl=CF_2$ | Peroxide | $SF_5CF_2CFCl_2$ (3) + much high-boiling material | 249 |
| | $CFCl=CF_2$ | UV | $SF_5CFClCF_2Cl$ (1) $ClCF_2CFCl_2$, $S_2F_{10}$ + much high-boiling material | 249 |
| | $CHF=CF_2$ | Peroxide | $SF_5CHFCF_2Cl$ (62) | 249 |
| | $HC≡CH$ | UV | $SF_5CH=CHCl$ (—) | 246 |
| | $CH_2=CHCl$ | None added | $SF_5CH_2CHCl_2$ (37) | 248 |
| | $CH_2=CH_2$ | None added | $SF_5CH_2CH_2Cl$ (47) $SF_5(CH_2CH_2)_2Cl$ (8) | 248 |
| | $CF_2=CFCF_3$ | UV | $SF_5CF_2CFClCF_3$ $SF_5CF(CF_3)CF_2Cl$ (20) | 249 |
| | $HC≡CCH_3$ | UV or none | $S_2F_{10}$, $CF_3CFClCF_2Cl$ | 248 |
| | $CH_2=CHCH_3$ | UV or none | $SF_5CH=CClCH_3$ (25) | 248 |
| | $CH_2=CHCH=CH_2$ | None added | $SF_5CH_2CHClCH_2$ (78) $SF_5CH_2CHClCH=CH_2$ (37) | 248 |

| | | | |
|---|---|---|---|
| Unsaturate | | Conditions | Product |

| | | | |
|---|---|---|---|

CH₂=CHCH₂H, n

CH₃CH₂CH₂CH₂CH₃



C₅H₅C(=O)—NC₄H₈
       |
       Cl

CF₂=CF₂
CH₃CO₂CH=CH₂

CH₃NCH₃
(= C₅H₁₁N₂)

None added

None added

None added

UV

Iodine

UV

H₂S (5)
(C₂H₁₁)₂S (33)
(C₂H₁₁)₂S₂ (12)
(C₄H₁₁)₂S₄ (22)
H₂S (33)
(C₂H₁₁)₂S (16)
(C₄H₁₁)₂S (8)
(C₅H₁₁)₂S₂ (19)
S (16)

Br₂S (30)

   (8)

S₅ (7)

   C₂H₅C=CH

C=NC₅H₁₀ (80)

CH₂SₙCF₂(CF₂)ₙSC₅H₅ (—)
CH₂CO₂CH[SC₅H₅ ₙ)CH₂SC₄H₅, n (30)

255, 254

255

255

578

87
76

*Note*   References 342 to 631 are on pp. 571–578.
† No structure was given for this product.

## TABLE XI

### ADDITION OF SILANES TO OLEFINS AND ACETYLENES

#### A. Trichlorosilane and Olefins

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| CF₂=CFCl | Peroxide | (C₂HF₃Cl)SiCl₃ (38) | 266 |
| | UV | CHFClCF₂SiCl₃ (45) | 281 |
| | UV | (C₂HF₃Cl)SiCl₃ (19) | 266 |
| | Thermal (~200°) | CHFClCF₂SiCl₃ ⎱ CHF₂CFClSiCl₃ ⎰ CF₂=CFSiCl₃ | 279, 280 |
| CF₂=CCl₂ | Ozone | (C₂HF₃Cl)SiCl₃ (30) | 270 |
| CFCl=CFCl | Thermal (450°) | CFCl=CFSiCl₃ | 279 |
| CCl₂=CCl₂ | Thermal (450°) | CFCl=CFSiCl₃ ⎱ CHCl₂CCl₂SiCl₃ (1) ⎰ | 280 |
| | UV | CCl₃CCl₂SiCl₃ (7) | 297 |
| | Peroxide | CHCl₂CCl₂SiCl₃ (2-5) ⎱ CCl₂=CClSiCl₃ (11-13) ⎰ | 297 |
| CF₂=CF₂ | Thermal (300-600°) | CCl₂=CClSiCl₃ (14) | 297, 294 |
| | UV | CHF₂CF₂SiCl₃ (44-58) + higher telomers | 277 |
| | Thermal (200°) | CHF₂CF₂SiCl₃ | 279 |
| | Ozone | CHF₂CF₂SiCl₃ (40) | 270 |
| CHCl=CCl₂ | Thermal (500°) | CCl₃=CHSiCl₃ | 295, 296 |
| CF₂=CHF | UV | CHF₂ClPSiCl₃ (50) | 281 |
| CHCl=CHCl | Thermal (600°) | CHCl=CHSiCl₃ (25) | 295 |
| | γ-Rays | CH₂ClCHClSiCl₃ (27) ⎱ CH₂Cl(CHCl)₃SiCl₃ (12) ⎰ | 260 |
| CH₂=CCl₂ | Thermal (550°) | (C₂H₃Cl)SiCl₃ (—) | 295 |
| CH₂=CHCl | Thermal (600°) | CH₂=CHSiCl₃ (53) | 272 |
| Cl₃SiCH=CH₂ | Peroxide | Cl₃SiCH₂CH₂SiCl₃ (19) | 257, 570 |
| CH₂=CH₂ | Thermal (300°) | Cl₃SiCH₂CH₂SiCl₃ (—) | 580 |
| | Peroxide | C₂H₅SiCl₃ (—) | 581 |
| | Azo | C₂H₅SiCl₃ (30-50) | 261 |
| | Thermal (285°) | H(C₂H₄)ₙSiCl₃ | 274, 273, 275, 292, 582, 583 |
| | | n = 1 (20) | |
| | | n = 2 (26) | |
| | | n = 3 (15) | |
| | | n = 4 (13) | |
| | | n = 5 (4) | |
| | | n > 5 (12) | |

|  | Aro/lugh pressure | H(CH₂)ₐSCₐ | 261 |
|---|---|---|---|
|  |  | n = 1 (13) |  |
|  |  | n = 2 (9) |  |
|  |  | n = 3 (4) |  |
|  |  | n > 3 (15) |  |
| CF₃CCl=CCl₂ | UV | CF₃CH₂Cl)·CCl₃ (9) | 266 |
| CF₂=CF₂ | Peroxide | CF₃(CH₂Cl)·CCl₃ (34) | 266 |
| CF₃CH=CH₂ | UV | CF₂CHCl·CCl₃ (1) | 266 |
|  | Peroxide | CF₃CClF·CCl₃ (1) | 266 |
| CH₂ClCH=CH₂ | Thermal (200-300°) | CF₃CH(CF₂)·CCl₃ (11) | 266 |
|  | Peroxide | CF₂CH(CF₂)·CCl₃ (52-91) | 266, 262 |
|  | UV | CH₂CH(CH₂)·CCl₃ (15) | 266 |
|  | γ-Rays | CH(CH₂)·NCl₃ (20) | 259 |
|  | Peroxide | CH(CH₃)·NCl₃ (24) | 259 |
|  | γ-Rays | HCCH₂(CH₂)·CCl₃ (40) | 261 |
| CH₂S.CH=CH₂ | Peroxide | C₃H₆Cl(CH₂)·CCl₃ (33-42) | 257, 259 |
| CH₂CH—CH₂ |  | n C₃H₆SC₂ (63-90) | 2, 3 |
| C₄F₇CH=CH₂ | Thermal (360°) | C₂H₅(CHF)·NCl₃ (—) | 5, 3, 292 |
| C₄F₂CF=CF₂ | Thermal (200°) | CₙCH₂(CHF)·N·Cl₃ (—) | 259 |
| C₄F₂CF=CF₂ | Thermal (200-250°) | C₂H₅CClF·NCl₃ (20) | 272, 259 |
| CF₃CH—CH₂ | UV | CF₂CHCl·NCl₃ (29) | 266 |
| NCClCH—CH₂ | Peroxide | CF₂CH(CF₂)·Cl₂ (22) | 266 |
| CF₂=CHCH=CH₂ | γ-Rays | CF₂CH(CF₂)·Cl₃ (40) | 266 |
|  | γ-Rays | N(CH₂)·N·Cl₃ (8) | 260 |
| CH₂CO.CH=CH₂ | Aso | CH(CHCl)·N₃ (—) | 261 |
| C₆H₅CH=CH₂ | Thermal (330°) | CH₂·CH(CH₂)·N·Cl₃ (10) | 258 |
| (CH₃)₂C=CH₂ | Peroxide | CH₂·CH₂(CH₂)·NCl₃ (10) | 258 |
|  | Thermal (280°) | (CH₃)₂CHCH₂·NCl₂ (78-82) | 292, 293 |
|  | Thermal (280°) | (CH₃)₂CHCH₂·NCl₂ (6-11) | 292, 293 |
| CH₂CH=CHCH₃ | Thermal | (CH₃)₂CHCH(SiCl₃)·H (10) | 292, 281 |
| C₆H₅CH=CH₂ | Peroxide | C₆H₅CH₂·SiCl₃ (61) | 259 |
|  | Thermal (280°) | C₆H₅CH(CH₃)·SiCl₃ (93) | 260 |
|  | γ-Rays | C₆H₅CH(CH₃)·SnCl₃ (—) | 563, 292 |
|  | UV | CₙHₙ(OH)·N₃ (—) | 260 |
|  | UV | C₆H₅OH(CH₂)₂·N₃ (52) | 565 |
|  |  |  | 565 |

Note.—References 365 to 631 are on pp. 371-376.
* The figures are parts by weight, not percentages.

## TABLE XI—Continued

### A. Trichlorosilane and Olefins—Continued

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| $C_3F_7CH=CH_2$ | γ-Rays | $C_3F_7CH_2CH_2SiCl_3$ (52) | 260 |
| $C_2F_5C(CH_3)=CH_2$ | γ-Rays | $C_2F_5CH(CH_3)CH_2SiCl_3$ (9) | 260 |
| [cyclopentene] | Thermal (280°) | $Cl_3Si$[cyclopentyl]$SiCl_3$ (45) | 586 |
| [cyclopentene] | Thermal (280°) | [cyclopentyl]$SiCl_3$ (59) | 292 |
| | γ-Rays | [cyclopentyl]$SiCl_3$ (96) | 260 |
| $CH_3CO_2CH_2CH=CH_2$ | γ-Rays | $CH_3CO_2(CH_2)_3SiCl_3$ (22) | 260 |
| | | $H(CH_3CO_2C_3H_6)_3SiCl_3$ (71) | 263 |
| $C_3H_7CH=CH_2$ | Peroxide | $n$-$C_5H_{11}SiCl_3$ (0–100)† | 292 |
| | Thermal (280°) | $n$-$C_5H_{11}SiCl_3$ (76) | 257, 581 |
| | Peroxide | $n$-$C_5H_{11}SiCl_3$ (44) | 292, 582 |
| $C_2H_5CH=CHCH_3$ | Thermal (290°) | $n$-$C_3H_7CH(CH_3)SiCl_3$ (70) | 263 |
| | Peroxide | $n$-$C_3H_7CH(CH_3)SiCl_3$ (70:30)‡ | |
| | | $C_2H_5CH(C_2H_5)SiCl_3$ } | 587 |
| $(CH_3)_2CHCH=CH_2$ | Peroxide | $(CH_3)_2CHCH_2CH_2SiCl_3$ (5–11) | 259 |
| $(CH_3)_2C=CHCH_3$ | Peroxide | $C_5H_{11}SiCl_3$ (25) | 292 |
| | Thermal (280°) | $(CH_3)_2CHCH(CH_3)SiCl_3$ (78) | 259 |
| | UV | $C_5H_{11}SiCl_3$ (64) | 260 |
| | γ-Rays | $C_5H_{11}SiCl_3$ (94) | 585 |
| $C_3H_5OCH_2CH=CH_2$ | UV | $C_3H_5O(CH_2)_3SiCl_3$ (84) | 588, 287 |
| $(CH_3)_3SiCH=CH_2$ | Peroxide | $(CH_3)_3SiCH_2CH_2SiCl_3$ (70–90) | 260 |
| $C_3F_7C(CH_3)=CH_2$ | γ-Rays | $C_3F_7CH(CH_3)CH_2SiCl_3$ (11) | |
| [cyclohexene] | Thermal (280°) | cyclo-$C_6H_{11}SiCl_3$ (45) | 586 |

| Reactant | Conditions | Products | References |
|---|---|---|---|
| (cyclohexene) | Peroxide | $C_6H_{11}SiCl_3$ (30–46) | 257, 541, 262, 293 |
| | Azonitrile | $C_6H_{13}SiCl_3$ (35–73) | 262 |
| | χ Rays | $CH_3(CH_2)_7SiCl_3$ [9] | 262, 542 |
| | Thermal (290–325°) | $C_6H_{13}SiCl_3$ [28] | 293 |
| | | $C_6H_{13}SiCl_3$ [21] | |
| $CH_3$—CH(CH_3)CH_2CH=CH_2 (CH_3) | UV | (cyclohexene)SiCl_3 (14) | 254 |
| $n$-$C_6H_{13}CH=CH_2$ | Thermal (280°) | $C_2H_5CH(CH_3)SiCl_3$ (70) | 256 |
| $n$-$C_6H_{13}CH=CH_2$ | Thermal (290°) | $Cl_3Si$—CH(CH_3)CH_2SiCl_3 (23) | 256, 542 |
| $n$-$C_6H_4(CH)CH=CH_2$ | Thermal (290°) | $n$-$C_6H_{11}SiCl_3$ (42) | 542 |
| | Thermal (290°) | $Cl_3Si(CH_2)_4SiCl_3$ (45) | 255 |
| | | $n$-$C_6H_{13}CHClSiCl_3$ (62) | 255 |
| (CH_3)_2C=CH—CH=CH_2 | Azonitrile | $n$-$C_6H_{13}CH_2CH_2SiCl_3$ (—) | 261 |
| (CH_3)_2C=C(CH_3)_2 | Thermal (280°) | (Cl_3Si)_2CHCH_2CH_2CH_2SiCl_3 (60) | 262 |
| | Peroxide | (Cl_3Si)_2CHCH(CH_3)CH_3SiCl_3 (55) | 262 |
| | Peroxide | (Cl_3Si)_2CHCH(CH_3)CH_2SiCl_3 (29) | 262 |
| | Peroxide | (Cl_3Si)_2CHCH_2CH_2CH_2SiCl_3 (12) | 542 |
| | Peroxide | (Cl_3Si)_2Si(CH_3)_2SiCl_3 (3) | 553 |
| | | | 253 |
| (cyclohexene) (CH_3) | γ-Rays | $C_6H_{11}SiCl_3$ (92) | 260 |
| (CH_3)_3SiCH=CH_2 | Thermal (280°) | $n$-$C_6H_{13}SiCl_3$ (60) | 292 |
| (C_2H_5O)_3SiCH=CH_2 | Peroxide | $C_6H_{13}CH_2(CH_3)SiCl_3$ (47) | 306 |
| | | ($n$-$C_6H_{13}CHSiCl_3$) | |

Note. References 383 to 631 are on pp. 371–376.
* The reactions were run in the presence of a large variety of additives with resultant variations in yield.
† The mixture was separated, but individual compounds were not differentiated.

## TABLE XI—Continued
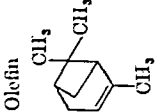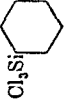
### A. Trichlorosilane and Olefins—Continued

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| C₆H₅CH=CH₂ | Azonitrile | H(C₈H₈)₄SiCl₃ | 261 |
| | Thermal (350°) | C₈H₉SiCl₃ (30) | 582 |
| | Peroxide | H(C₈H₈)₂SiCl₃ (7) | 589 |
| | | H(C₈H₈)ₙSiCl₃ (>80) (average value of n = 59) | |
| [cyclohexenyl]–CH=CH₂ | Thermal (330°) | [cyclohexyl]–CH₂CH₂SiCl₃ (with SiCl₃) (21) | 258, 590 |
| n-C₆H₁₃CH=CH₂ | Peroxide | n-C₈H₁₇SiCl₃ (99) | 256, 259 |
| | UV | n-C₈H₁₇SiCl₃ (31–47) | 259 |
| | Thermal (290°) | n-C₈H₁₇SiCl₃ (80–94) | 583, 292 |
| | Azonitrile | n-C₈H₁₇SiCl₃ (75) | 261 |
| | γ-Rays | n-C₈H₁₇SiCl₃ (99) | 260 |
| n-C₅H₁₁CH=CHCH₃ | Peroxide | C₈H₁₇SiCl₃ (99) | 259 |
| n-C₅H₁₁C(CH₃)=CH₂ | Peroxide | n-C₅H₁₁CH(CH₃)CH₂SiCl₃ (70) | 259 |
| (CH₃)₃CCH₂C(CH₃)=CH₂ | Peroxide | (CH₃)₃CCH₂CH(CH₃)CH₂SiCl₃ (9) | 259 |
| | Azonitrile | (CH₃)₃CCH₂CH(CH₃)CH₂SiCl₃ (30) | 261 |
| | Thermal (280°) | (CH₃)₃CCH₂CH(CH₃)CH₂SiCl₃ (7) | 292 |
| | | (CH₃)₂C=CHSiCl₃ (36) | |
| | | (CH₃)₃CCH(C₃H₇-i)SiCl₃ (18) | |
| (CH₃)₃CCH=C(CH₃)₂ | Peroxide | C₈H₁₇SiCl₃ (0) | 259 |
| | Thermal (300°) | (CH₃)₃CCH(C₃H₇-i)SiCl₃ (—) | 258 |
| (C₂H₅)₃SiCH=CH₂ | Peroxide | (C₂H₅)₃SiCH₂CH₂SiCl₃ (42) | 588 |
| [bicyclic]–CO₂CH₃ | Peroxide | Cl₃Si–[bicyclic]–CO₂CH₃ (—) | 591 |
| n-C₇H₁₅CH=CH₂ | Thermal (280°) | n-C₉H₁₉SiCl₃ (89) | 292 |
| | Peroxide | n-C₉H₁₉SiCl₃ (61) | 587 |

| | | | | References |
|---|---|---|---|---|
| $(C_6H_5)_3Si(CH_2)_3CH=CH_2$ | Peroxide | $(C_6H_5)_3Si(CH_2)_5SiCl_3$ (10) | | 293 |
| | Thermal (280°) | $Cl_3SiC_6H_5$ (29) | | 506 |
| $CH_3SiCH_2CH=CH_2$ | UV | $CH_3CH(CH_2CH_2SiCl_3$ (—) | | 532 |
| $CH_3Si(CH_3)_2CH=CH_2$ | Peroxide | $C_6H_5Si(CH_2CH_2CH_2SiCl_3$ (24) | | 544 |
| $CH_2=C(CH_3)CH=CH_2$ | Thermal (280°) | $CH_3CH(CH_3)_4$ (68) | | 546 |
| | UV | $CH_3CH(CH_2)_2NaCl_4$ (59) | | |
| | | $CH_2CH(CH_2)_2CH(CH_2)_2SiCl_4$ (—) | | 272 |
| | Peroxide | $CH_2CH(CH_2)_4CH(CH_2)_2SiCl_4$ (33) | | 229 |
| $CH(CH_3)_4$ | Peroxide | $CH(CH_3)_4$ (49) | | 299, 631, 301, 302 |
| | | $CH_3SiCl_3$ | | |
| $CH(CH_3)_4$ | UV | $CH(CH_3)_4$ (—) | | 300 |
| | | $SiCl_3$, $CH_3SiCl_3$ | | |

Note. References 385 to 631 are on pp. 371–376.

## TABLE XI—Continued

### A. Trichlorosilane and Olefins—Continued

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| (structure: bicyclic, CH₃, CH₃, CH₃) | Peroxide | C₁₀H₁₇SiCl₃ (56) | 299 |
| (structure: cyclohexene, (CH₃)₂, =CH₂) | Peroxide | C₁₀H₁₇SiCl₃ (22) | 299 |
| | Thermal (280°) | C₁₀H₁₇SiCl₃ (69) | 292 |
| n-C₈H₁₇CH=CH₂ | Thermal (290°) | n-C₁₀H₂₁SiCl₃ (60–90) | 583, 292 |
| | Peroxide | n-C₁₀H₂₁SiCl₃ (63) | 587 |
| CH₂=CH(CH₂)₈COCl | UV | Cl₃Si(CH₂)₁₀COCl (—) | 594 |
| C₆H₅Si(CH₃)₂CH₂CH=CH₂ | Peroxide | C₆H₅Si(CH₃)₂(CH₂)₈SiCl₃ (22) | 293 |
| CH₂=CH(CH₂)₈CO₂CH₃ | Peroxide | Cl₃Si(CH₂)₁₀CO₂CH₃ (—) | 595 |
| n-C₁₀H₂₁CH=CH₂ | Thermal (290°) | n-C₁₂H₂₅SiCl₃ (84–95) | 583, 292 |
| [(CH₃)₃CCH₂]₂C=CH₂ | Peroxide | C₁₂H₂₅SiCl₃ (2) | 259 |
| (structure: cyclohexene, CO₂C₂H₅, CO₂C₂H₅) | Peroxide | Cl₃Si (structure, CO₂C₂H₅, CO₂C₂H₅) (—) | 591 |
| n-C₁₂H₂₅CH=CH₂ | Thermal (280–315°) | n-C₁₄H₂₉SiCl₃ (88) | 292, 583 |
| (n-C₄H₉)₃SiCH=CH₂ | Peroxide | (n-C₄H₉)₃Si(CH₂)₂SiCl₃ (13) | 293 |
| n-C₁₄H₂₉CH=CH₂ | Thermal (290°) | n-C₁₆H₃₃SiCl₃ (93) | 292, 258 |
| | Peroxide | n-C₁₆H₃₃SiCl₃ (30) | 587 |
| n-C₁₆H₃₃CH=CH₂ | Thermal (300°) | n-C₁₈H₃₇SiCl₃ (88–94) | 258, 583 |
| | Azonitrile | n-C₁₈H₃₇SiCl₃ (98) | 261 |
| CH₃(CH₂)₇CH=CH(CH₂)₇CO₂CH₃ | UV | C₁₉H₃₇O₂SiCl₃ (22) | 596 |

## B. Methyldichloroamines and Olefins
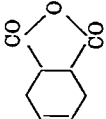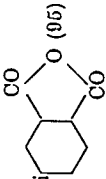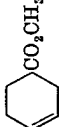
| Olefin | Catalyst | Products (%) | Refs. |
|--------|----------|-------------|-------|
| $CF_2=CFCl$ | Thermal (440–490°) | $CF_3CFClN(CH_3)_2$ (—) | 279, 280 |
| $CFCl=CFCl$ | Thermal (440–490°) | $CFCl_2CFClN(CH_3)_2$ (—) | 280 |
| $CF_2=CCl_2$ | Thermal (450–600°) | $CF_3CCl_2N(CH_3)_2$ (—) | 279 |
| $CCl_2=CCl_2$ | Thermal (300°) | $CCl_3CCl_2N(CH_3)_2$ (—) | 257 |
| | Peroxide | $CCl_3=CClN(CH_3)_2$ (—) | 257 |
| $CF_2=CF_2$ | Thermal (550–600°) | $CClF_2CF_2N(CH_3)_2$ (4–19) | 594 |
| $=as$ $CH_2=CHCl$ | Thermal (350–600°) | $CH_3=CHN(CH_3)_2$ (—) | 591 |
| $CF_2=CH_2$ | Thermal (350–600°) | $CHCl_2=CH_2N(CH_3)_2$ (—) | 597 |
| | Thermal (550–600°) | $CH_3=CHClCH_2N(CH_3)_2$ (20) | 272, 597 |
| $CH_3=CH=CH_2$ | Peroxide | $H(CH_2)_4N(CH_3)_2X_2$ (—) | 595 |
| $CH_3=CH_2$ | Thermal (300°) | $n = 1$ (24) | 275 |
| | | $n = 2$ (36) | |
| | | $n = 3$ (11) | |
| | | $n = 4$ (6) | |
| | | $n = 5$ (3) | |
| | | $n = 6$ (2) | |
| | | $n = 8$ (4) | |
| $CF_3CCl=CCl_2$ | Thermal (300°) | $C_6H_5N(CH_3)_2X$ (—) | 594 |
| $CF_3CF=CF_2$ | Fe(CO)$_5$ | $C_6H_5=N(CH_3)_2X$ (70) | 264 |
| | Peroxide | $C_6H_5=N(CH_3)_2CCl_3$ (23) | 260 |
| | Thermal (470–490°) | $CF_3CF=CF_2N(CH_3)_2$ (—) | 280 |
| | | $CF_3CF=CF_2N(CH_3)_2X_2$ (—) | |
| $\gamma$ Rays | | $HC_6H_5N(CH_3)_2Cl$ (4) | |
| $CF_3CH=CH_2$ | Peroxide | $CF_3(CH_2)_2N(CH_3)_2$ (11) | 263, 256 |
| $CH_3CH=CH_2$ | Thermal (300°) | $CF_3CH_2CH_2N(CH_3)_2$ (82) | 266 |
| | Thermal (300°) | $HC_6H_5N(CH_3)_2Cl$ (70) | 258 |
| | | $H(C_2H_4)_2N(CH_3)_2Cl$ (70) | 276, 272, |
| | | | 275 |
| $CH_3SO_2CH=CH_2$ | Fe(CO)$_5$ | $m-C_6H_4N(CH_3)_2Cl$ (70) | 261 |
| $C_6H_5CH=CH_2$ | Thermal (300°) | $H(C_2H_4)_2N(CH_3)_2Cl_2$ (—) | 550 |
| | UV | $CH_3SO_2CH_2CH_2N(CH_3)_2Cl$ (19) | 559 |
| | Peroxide | $C_6H_5CH=CH_2N(CH_3)_2Cl$ (44) | 266 |

Note. References 383 to 631 are on pp. 371–376.

## TABLE XI—*Continued*

### B. Methyldichlorosilane and Olefins—*Continued*

| Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|
| $CF_3C(CH_3)=CH_2$ | UV | $CF_3CH(CH_3)CH_2Si(CH_3)Cl_2$ (63) | 269 |
| $C_2H_5CH=CH_2$ | Thermal (300°) | $n\text{-}C_4H_9Si(CH_3)Cl_2$ (—) | 258 |
| $CH_3CH=CHCH_3$ | γ-Rays | $C_2H_5CH(CH_3)Si(CH_3)Cl_2$ (57) | 260 |
| $Cl_2(CH_3)SiCH_2CH=CH_2$ | Thermal (280°) | $Cl_2(CH_3)Si(CH_2)_3Si(CH_3)Cl_2$ (—) | 580 |
| ![structure] $\begin{matrix} & F_2 \\ & C \\ CF_2 & CCl \\ CF_2 & CCl \end{matrix}$ | Thermal (470–500°) | $\begin{matrix} & F_2 \\ & C \\ CF_2 & CCl \\ CF_2 & =CSi(CH_3)Cl_2 \end{matrix}$ (—) | 279, 280 |
| ![structure] $\begin{matrix} & F_2 \\ & C \\ CF_2 & CH \\ CF_2 & CCl \end{matrix}$ | Thermal (490–500°) | $\begin{matrix} & F_2 \\ & C \\ CF_2 & CH \\ CF_2 & =CSi(CH_3)Cl_2 \end{matrix}$ (—) | 280 |
| $n\text{-}C_3F_7CH=CH_2$ | γ-Rays | $C_3F_7(CH_2)_2Si(CH_3)Cl_2$ (23) | 260 |
|  | UV | $C_3F_7(CH_2)_2Si(CH_3)Cl_2$ (73) | 269 |
| $C_2F_5C(CH_3)=CH_2$ | γ-Rays | $C_2F_5CH(CH_3)CH_2Si(CH_3)Cl_2$ (2) | 260 |
| ⬠ | γ-Rays | $C_5H_9Si(CH_3)Cl_2$ (20) | 260 |
| $CH_3CO_2CH_2CH=CH_2$ | γ-Rays | $CH_3CO_2(CH_2)_3Si(CH_3)Cl_2$ (47) | 260 |
| $n\text{-}C_3H_7CH=CH_2$ | Peroxide | $n\text{-}C_5H_{11}Si(CH_3)Cl_2$ (10) | 257, 581 |
|  | Thermal (300°) | $n\text{-}C_5H_{11}Si(CH_3)Cl_2$ (—) | 258 |
| $C_2H_5CH=CHCH_3$ | Peroxide | $n\text{-}C_3H_7CH(CH_3)Si(CH_3)Cl_2$ (21) | 257, 581 |
| $(CH_3)_2C=CHCH_3$ | γ-Rays | $(CH_3)_2CHCH(CH_3)Si(CH_3)Cl_2$ (30) | 260 |
| $(CH_3)_3SiCH=CH_2$ | Peroxide | $(CH_3)_3Si(CH_2)_2Si(CH_3)Cl_2$ (74) | 287 |
| ⬡ | Thermal (300°) | $C_6H_{11}Si(CH_3)Cl_2$ (—) | 258 |
|  | γ-Rays | $C_6H_{11}Si(CH_3)Cl_2$ (45) | 260 |

| | Catalyst | Product (%) | Refs. |
|---|---|---|---|
| n-C₃F₇C(CH₃)=CH₂ | γ-Rays | C₃F₇CH(CH₃)CH₂Si(CH₃)₂CCl₃ (6) | 260 |
| n-C₃H₇CH=CH₂ | γ-Rays | n-C₃H₇CH₂CH₂Si(CH₃)₂CCl₃ (55) | 260 |
| n-C₄H₉CH=CH—CH₃ | Thermal | C₆H₁₃Si(CH₃)₂CCl₃ (21) | 598 |
| n-C₆H₁₃CH=CH₂ | Peroxide | | 587 |
| $CO_2CH_3$ (ring) | Peroxide | C₆H₅Si(CH₃)₃ | 591 |
| (bicyclic) | Peroxide | n-C₇H₁₅Si(CH₃)₂CCl₃ (38) | 587 |
| (bicyclic) | Peroxide | n-C₇H₁₅Si(CH₃)₂Cl (32) | 299 |
| $CH_3$ (ring) | Peroxide | C₆H₁₃Si(CH₃)₂Cl (18) | 299 |
| n-C₆H₁₃CH—CH—CH₂ | Peroxide | n-C₉H₁₉Si(CH₃)Cl (—) | 258 |

## C. Silane and Other Substituted Silanes and Olefins

| Silane | Olefin | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| SiH₄ | CH₂=CH₂ | Thermal (75–200°) | C₂H₅SiH₃, (—) | 236 |
| | CH₂=CH₂ | Thermal (450–510°) | H(C₂H₄)ₙSiH₃, (—) (n = 1, 2, etc.) | 271 |
| | CH₂=CH₂ | UV/flow system | C₂H₅SiH₃ (4) | 271 |
| | | | n-C₃H₇SiH₃ (5) | |
| | | | (C₂H₅)₂SiH₂ (5) | |
| C₆H₅SiH₃ | CH₃CH=CH₂, (CH₃)₂C=CH₂, CH₂=CHCH₃ | Thermal (100°) | n-C₃H₇(C₆H₅)SiH₂ (—) | 599, 286 |
| C₆H₅SiH₃ | CH₂=CH₂ | Thermal (75–200°) | (C₆H₅)₄Si (2) | 599, 286 |
| | | | (C₆H₅)₃SiH (30) | 270 |
| | | Ozone | (C₆H₅)₂SiH₂ (7) | 296 |
| n-C₆H₁₃SiH₃ | n-C₅H₁₁CH=CH₂ | Thermal (315°) | n-C₆H₁₃SiH₂C₇H₁₅ (60) | 278 |
| | | Peroxide | | |

*Note*  References 385 to 631 are on pp. 571–576.

TABLE XI—Continued

C. Silane and Other Substituted Silanes and Olefins—Continued

| Silane | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| $C_6H_5SiH_3$ | $CH_3CO_2CH_2CH=CH_2$ | Peroxide | $CH_3CO_2(CH_2)_3Si(C_6H_5)H_2$ (72–77) | 278, 600 |
| | (cyclohexene) | Peroxide | $C_6H_{11}Si(C_6H_5)H_2$ (25) | 278 |
| | $(CH_2=CHCH_2)_2O$ | Peroxide | $CH_2=CHCH_2O(CH_2)_3Si(C_6H_5)H_2$ (60) | 278 |
| | $(CH_3)_3SiOCH_2CH=CH_2$ | Peroxide | $(CH_3)_3SiO(CH_2)_3Si(C_6H_5)H_2$ (—) | 278, 600 |
| | $(CH_3OCO)_2CHCH=CH_2$ | Peroxide | $(CH_3OCO)_2CH(CH_2)_2Si(C_6H_5)H_2$ (38) | 278 |
| | $(C_2H_5O)_2CHCH=CH_2$ | Peroxide | $(C_2H_5O)_2CH(CH_2)_3Si(C_6H_5)H_2$ (55) | 278 |
| | (norbornene anhydride structure) | Peroxide | $H_2(C_6H_5)Si$ (structure) (95) | 278 |
| | (cyclohexene-$CO_2CH_3$ structure) | Peroxide | $H_2(C_6H_5)Si$ (structure) $CO_2CH_3$ (66) | 591, 278 |
| | $n\text{-}C_6H_{13}CH=CH_2$ | Peroxide | $n\text{-}C_8H_{17}Si(C_6H_5)H_2$ §<br>$(n\text{-}C_8H_{17})_2Si(C_6H_5)H$<br>$(n\text{-}C_8H_{17})_3SiC_6H_5$ | 278 |
| | $[(CH_3)_3Si]_2NCH_2CH=CH_2$ | Peroxide | $[(CH_3)_3Si]_2N(CH_2)_3Si(C_6H_5)H_2$ (81) | 601, 278 |
| | $o\text{-}CH_3CO_2C_6H_4CH_2CH=CH_2$ | Peroxide | $o\text{-}CH_3CO_2C_6H_4(CH_2)_3Si(C_6H_5)H_2$ (50) | 278 |
| | $CH_3O_2C(CH_2)_8CH=CH_2$ | Peroxide | $CH_3O_2C(CH_2)_{10}Si(C_6H_5)H_2$ (98) | 591 |
| | (bicyclic $CH_3CO_2$ structure) | Peroxide | (bicyclic structure) $Si(C_6H_5)H_2$ (79) | 600, 278 |
| | $CH_3CO_2(CH_2)_9CH=CH_2$ | Peroxide | $CH_3CO_2(CH_2)_{11}Si(C_6H_5)H_2$ (—) | 600 |
| | $(CH_3)_3SiNH(CH_2)_9CH=CH_2$ | Peroxide | $(CH_3)_3SiNH(CH_2)_{11}Si(C_6H_5)H_2$ (—) | 601 |
| | $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$ | Peroxide | $C_{17}H_{34}(CO_2CH_3)Si(C_6H_5)H_2$ (100) | 591, 278 |

| | | | | |
|---|---|---|---|---|
| ClC₆H₄SH₃ <br> (structure with CH₂N₃Si(CH₃)₂]₂) | CCl₄→CCl₃ <br> CF₂=CF₂ <br> CF₃CH=CH₂ <br> | Peroxide | $CH₂N₃Si(CH₃)₂]₂$ (−) | 601 |
| C₃AsH₃ | CCl₄→CCl₃ <br> CF₂=CF₂ <br> CF₃CH=CH₂ | Thermal (200°) <br> Thermal (200°) <br> Thermal (200°) | $CCl₃—(CCl₃)SiCl₃$ [—] <br> $(ClF₂CF₂)₃SiCl₃$ [—] <br> $(CF₃CH₂CH₂)₃SiCl₃$ (—) | 294 <br> 279 <br> 279 <br> 269 |
| (CH₃)₃SiH | CF₂=CF₂ | UV | $(CHF₂CF₂)₃Si(CH₃)₃H$ (—) | 207 |
| C₆H₁₁Si(CH₃)₃SiH₂ | CH₃O₂CCH₂CH=CH₂ | Peroxide | $H(CH₃)₃Si$ | 278 |
| (C₆H₁₁)₃SiH | CH₃O₂CCH₂CH=CH₂ | Peroxide | structure (CO) | 278 |
| Br₃SiH | n C₆H₁₃CH=CH₂ <br> (CH₃)₂CHCH=CH₂ <br> CH₃O₂CCH=CH₂ <br> (CH₃)₃N(CH₂)₃SiBr₃ | Peroxide <br> Peroxide <br> Peroxide | $n\ C₆H₁₃Si(C₆H₄)_3H$ (41) <br> $n\text{-}C₆H₁₃SiBr₃$ (70) <br> $CH₃O₂C(CH₂)₃SiBr₃$ (9) <br> $(CH₃)₃N(CH₂)₃SiBr₃$ | 602 <br> 258, 583 <br> 587 <br> 600 <br> 601 |
| | $C₆H₁₁SiBr₃$ (28) | Peroxide | | 288 |
| | structure with CH₃ | UV | $C₆H₁₁SiBr₃$ (70) | 288, 289 |
| | | UV | $C₇H₁₃(CH₃)SiBr₃$ (70) | 280 |
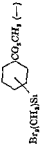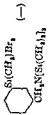
Note: References 355 to 631 are on pp 371–376.
§ The relative amounts of products are dependent on the ratio of reactants

## TABLE XI—Continued

### C. Silane and Other Substituted Silanes and Olefins—Continued

| Silane | Olefin | Catalyst | Products (%) | Refs. |
|---|---|---|---|---|
| Br₃SiH (contd.) | n-C₄H₉CH=CH₂ | UV | n-C₆H₁₃SiBr₃ (71) | 603 |
| | n-C₅H₁₁CH=CH₂ | UV | n-C₇H₁₅SiBr₃ (75) | 289 |
| | $\begin{array}{c}\text{CO}_2\text{CH}_3\end{array}$ (bicyclic) | Peroxide | Br₃Si-⟨⟩-CO₂CH₃ (82) | 278 |
| CH₃(SiHCl₂)₂ | n-C₇H₁₅CH=CH₂ | Peroxide | n-C₉H₁₉SiBr₃ (79) | 587 |
| Cl₃Si(C₂H₅)H | n-C₆H₁₃CH=CH₂ | Peroxide | n-C₁₀H₂₁SiBr₃ (74) | 587 |
| | n-C₄H₉CH=CH₂ | Peroxide | CH₃[Si(C₈H₁₇)Cl₂]₂ (22) | 289 |
| | CH₃CO₂CH=CH₂ | Peroxide | CH₃CO₂CH₂CH₂Si(C₂H₅)Cl₂ (10) | 584 |
| | (cyclohexene) | Peroxide | C₆H₁₁Si(C₂H₅)Cl₂ (11) | 288 |
| Cl₃Si(C₃H₇)H | CH₃O₂C(CH₂)₈CH=CH₂ | UV | CH₃O₂C(CH₂)₁₀Si(C₃H₇)Cl₂ (32) | 604 |
| Cl₃(n-C₄H₉)SiH | Cl₂(C₃H₇)SiCH=CH₂ | Thermal (300°) | Cl₂(C₃H₇)Si(CH₂)₂Si(C₃H₇)Cl₂ (—) | 580 |
| | CH₂=CH₂ | Thermal (300°) | n-C₄H₉Si(C₃H₇)Cl₂ + high-boiling material (25) | 582 |
| Cl₂(CF₃CH₂CH₂)SiH | CF₃CH=CH₂ | UV | (CF₃CH₂CH₂)₂SiCl₂ (85) | 269 |
| Cl₂(C₆H₅)SiH | (F₂, Cl, Cl cyclohexane) | Thermal (400–500°) | (F₂, Cl, Si(C₆H₅)Cl₂ structure) | 280 |
| | CH₂=CHCl | Thermal (550°) | CH₂=CHSi(C₆H₅)Cl₂ (—) | 272 |
| | CH₂=CH₂ | Thermal (290°) | H(C₂H₄)ₙSi(C₆H₅)Cl₂ (—) (n = 1, 2, 3) | 605, 273, 275, 598 |
| | CH₃CH=CH₂ | Thermal (225–250°) | n-C₃H₇Si(C₆H₅)Cl₂ (—) | 258, 598 |

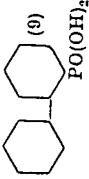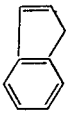| | | | | |
|---|---|---|---|---|
| Br₃(CH₃)SiH | [cyclohexene]—CO₂CH₃ | Peroxide | [cyclohexane]CO₂CH₃, (—) | 601 |
| Br₂(CH₃)₂Si | [bicyclic]CO₂CH₃, CO₂CH₃ | Peroxide | Br₂(CH₃)₂Si[...], (—) | 591 |
| [(CH₃)₂Si]₂NCH₂CH=CH₂ | | Peroxide | [(CH₃)₂Si]₂N(CH₂)₃Br₂, (—) | 601 |
| [cyclohexyl]CH₂N[Si(CH₃)₃]₂ | | Peroxide | Si(CH₃)₃Br₂ [cyclohexyl], (—) | 601 |
| | | Peroxide | C₆H₅Si(C₂H₅)₃Br₂, (44) | 288 |
| Cl(C₂H₅)₂SiH | CH₃CH₂CH₃ | Thermal (225–250°) | n-C₄H₉Siₓ(CH₃)ₓCl (—) | 256, 598 |
| Cl(C₂H₅)₂Si[CH₃]₃SiH | CH₂ClCCH₂·CH—CH₃ | UV | CH₂Cl₂CH₂Si(CH₃)₃, CH—CH₃ | 596, 604 |
| (CH₃)₃SiH | CH₂Cl·CH—CH₂ | Thermal (225–250°) | n-C₆H₁₃Si(CH₃)₃Cl (24–40) | 259 |
| CF₂=CF—CF₃ | CH₂ClCH=CH₂ | Thermal (225–250°) | n-C₆H₁₃Si(CH₃)₂Cl (—) | 258 |
| CF₃CF=CF₂ | CF₂=CF—CF₃ | Thermal (250°) | n-C₆H₁₃Si(C₂H₅)₂Cl (—) | 279 |
| CH₂=CH₂·CH₂SiH | CH₂=CH₂ | UV | (CH₃)₃SiCF₂CF₂CH₂CF₂CF₂ | 287 |
| (C₆H₅)₃SiH·OₓSiH | | Fe(CO)₅ | n-C₆F₉CH₂CH₂Si(CH₃)₂CH₃, (78) | 269 |
| (C₄H₉)₃SiH | | Thermal (300°) | (C₂H₅)₃Si (36) | 264 |
| | | | (C₆H₅)₃Si (11) | |
| | | | (C₆H₅)₃SiC₆H₅ | |
| (C₂H₅O)₃SiH | C₂H₅OCH=CH₂ | Fe(CO)₅ | (C₆H₅)₃SiC₂H₅ (6) | 602, 273, 275 |
| (n-C₄H₉)₃SiH | CH₂=CH₂ | Fe(CO)₅ | ...and higher telomers (C₆H₅)₃SiCH(CH₃)CH₂CH₃ (—) | 264 |
| | | Thermal (330°) | (C₆H₅)₃SiC₆H₅ (—) | 264 |
| | | | (n-C₄H₉)₃Si(CH₂CH₂)ₙH (—) (n = 3, 4, 6) | 582 |

Note: References 385 to 691 are on pp. 371–376.

TABLE XI—Continued

C. Silane and Other Substituted Silanes and Olefins—Continued

| Silane | Olefin | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $(C_6H_5)_3SiH$ | $(CH_3)_3SiCH_2CH=CH_2$ | Peroxide | $(CH_3)_3Si(CH_2)_3Si(C_6H_5)_3$ (3) | 293 |
| | $n\text{-}C_4H_9CH=CH_2$ | Peroxide | $n\text{-}C_6H_{13}Si(C_6H_5)_3$ (54) | 265 |
| | $n\text{-}C_8H_{17}CH=CH_2$ | Peroxide | $n\text{-}C_{10}H_{21}Si(C_6H_5)_3$ (25) | 603 |
| | $HO_2C(CH_2)_8CH=CH_2$ | Peroxide | $HO_2C(CH_2)_{10}Si(C_6H_5)_3$ (96) | 606 |
| | $C_{10}H_{21}CH=CH_2$ | Peroxide | $n\text{-}C_{12}H_{25}Si(C_6H_5)_3$ (46) | 291 |
| | $C_2H_5O_2C(CH_2)_8CH=CH_2$ | Peroxide | $C_2H_5O_2C(CH_2)_{10}Si(C_6H_5)_3$ | 606 |
| | $C_{12}H_{25}CH=CH_2$ | Peroxide | $n\text{-}C_{14}H_{29}Si(C_6H_5)_3$ (52) | 291 |
| | $C_{14}H_{29}CH=CH_2$ | Peroxide | $n\text{-}C_{16}H_{33}Si(C_6H_5)_3$ (45) | 291 |
| | $C_{16}H_{33}CH=CH_2$ | Peroxide | $n\text{-}C_{18}H_{37}Si(C_6H_5)_3$ (40) | 291 |
| | $(C_6H_5)_3SiCH_2CH=CH_2$ | Peroxide | $(C_6H_5)_3Si(CH_2)_3Si(C_6H_5)_3$ (36) | 293, 312 |

D. Silanes and Acetylenes

| Silane | Acetylene | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $Cl_3SiH$ | $HC{\equiv}CH$ | Peroxide | $Cl_3Si(CH_2)_2SiCl_3$ (3) | 257, 607 |
| | | Hot tube | $Cl_3SiCH=CH_2$ (—) | 295 |
| | $n\text{-}C_3H_7C{\equiv}CH$ | Peroxide | $n\text{-}C_3H_7CH=CHSiCl_3$ (38) | 283, 285 |
| | | Peroxide | $n\text{-}C_3H_7CH=CHSiCl_3$ (20) | 282 |
| | | Thermal | $n\text{-}C_3H_7CH=CHSiCl_3$ (—) | 582 |
| | | UV | $n\text{-}C_3H_7CH=CHSiCl_3$ (—) | 582 |
| | $i\text{-}C_3H_7C{\equiv}CH$ | Peroxide | $i\text{-}C_3H_7CH=CHSiCl_3$ (37) | 285 |
| | $n\text{-}C_4H_9C{\equiv}CH$ | Thermal | $n\text{-}C_4H_9CH=CHSiCl_3$ (15) | 608 |
| | $t\text{-}C_4H_9C{\equiv}CH$ | Peroxide | $t\text{-}C_4H_9CH=CHSiCl_3$ (36) | 283, 285 |
| | | Peroxide | $t\text{-}C_4H_9CH=CHSiCl_3$ (39) | 285 |
| | $(CH_3)_3SiC{\equiv}CCH_3$ | Peroxide | $(CH_3)_3SiC(SiCl_3)=CHCH_3$ (—) | 284 |
| | $n\text{-}C_5H_{11}C{\equiv}CH$ | Peroxide | $n\text{-}C_5H_{11}CH=CHSiCl_3$ (47) | 283, 285 |

*Note:* References 385 to 631 are on pp. 371–376.

TABLE XII

Addition of Germanes to Unsaturates

| Germane | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| Cl₃GeH | HC≡CH | None added | Cl₃GeCH₂CH₂GeCl₃, (90) | 315 |
| | CH₂=CH₂ | None added | CH₃CH₂GeCl₃, (55) | 315 |
| | CH₂=CHCl | None added | ClCH₂CH₂GeCl₃ (33) | 315 |
| | CHCl=CHSiCl₃ | None added | Cl₃SiCH₂CHClGeCl₃ (52) | 315 |
| | CH₂=CHSiCl₃ | None added | Cl₃SiCH₂CH₂GeCl₃ (53) | 315 |
| | CH₂=CHCH₂Cl | None added | NCCl₃(CH₂GeCl₃) (87) | 315 |
| | n-C₃H₇CH=CH₂ | None added | CH₃(CH₂)₄GeCl₃ (77) | 315 |
| | CH₂=CHCH₂COOH | None added | Cl₃GeCH₂CH₂CH₂COOH, (58) | 315 |
| | CH₂=CHCH₂CH₂Cl | None added | C₄H₈(GeCl₃)Cl (21) | 609 |
| | Diisobutylene | Peroxide | Cl₃GeCH₂CH(CH₃)CH₂C(CH₃)₃, (11) | 609 |
| | Chlorohexene | Peroxide | C₆H₁₂(GeCl₃)Cl (10) | 609 |
| | n-C₃H₇CH=CH₂ | Peroxide | C₅H₁₁GeCl₃ (22) | 609 |
| | n-C₄H₉CH=CH₂ | Peroxide | C₆H₁₃GeCl₃ (16) | 609 |
| | n-C₆H₁₃CH=CH₂ | Peroxide | C₈H₁₇GeCl₃ (18) | 609 |
| | n-C₈H₁₇CH=CH₂ | Peroxide | C₁₀H₂₁GeCl₃ (10) | 609 |
| | CH₂=CHCH₂OH | None added | (C₂H₅)₃GeCH₂CH₂CH₂OH, (11–22) | 610, 609 |
| | CH=CHC₆H₅ | None added | (C₂H₅)₃GeCH₂CH₂C₆H₅ (55) | 315 |
| | CH₂=CHCH₂OH | None added | (C₂H₅)₃GeCH₂CH₂CH₂OH (36) | 609 |
| | CH=CHCN | None added | (C₂H₅)₃GeCH₂CH₂CN (9) | 310 |
| | CH₂=CHCN | None added | (n-C₄H₉)₃GeCH₂CH₂CN, (31) | 310 |
| | CH₂=CHCH₂CH₂OH | None added | (n-C₄H₉)₃GeCH₂CH₂CH₂CH₂OH (—) | 310 |
| | CH₂=CHCN | None added | (n-C₄H₉)₃GeCH₂CH₂CN (—) | 310 |
| | | | (n-C₄H₉)₃GeCH₂CH₂CH₂OH (—) | 310 |
| | | | (n-C₄H₉)₃GeCH₂CH₂CN (—) | 310 |
| | | Peroxide or UV | 1:1 adduct and (C₆H₅)₃Ge— (—) | 314 |
| (C₆H₅)₃GeH | n-C₄H₉CH=CH₂ | Peroxide | n-C₆H₁₃Ge(C₆H₅)₃ (91) | 314 |
| (n-C₄H₉)₃GeH | n-C₆H₅CH=CH₂ | UV | n-C₆H₅Ge(C₄H₉)₃ (80) | 314 |
| (n-C₄H₉)₃GeH | n-C₃H₇CH=CH₂ | Peroxide | n-C₅H₁₁Ge(C₄H₉)₃ (60) | 311 |
| (C₆H₅)₃GeH | CH₂=CHSn(CH₃)₃ | Peroxide | (C₆H₅)₃GeCH₂CH₂Sn(CH₃)₃ (87) | 312 |
| | CH=CHSn(C₆H₅)₃ | Peroxide | (C₆H₅)₃GeCH₂CH₂Sn(C₆H₅)₃ (78) | |

## TABLE XI—Continued

### C. Silane and Other Substituted Silanes and Olefins—Continued

| Silane | Olefin | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $(C_6H_5)_3SiH$ | $(CH_3)_3SiCH_2CH=CH_2$ | Peroxide | $(CH_3)_3Si(CH_2)_3Si(C_6H_5)_3$ (3) | 293 |
| | $n\text{-}C_6H_{11}CH=CH_2$ | Peroxide | $n\text{-}C_8H_{17}Si(C_6H_5)_3$ (54) | 265 |
| | $n\text{-}C_{10}H_{21}CH=CH_2$ | Peroxide | $n\text{-}C_{10}H_{21}Si(C_6H_5)_3$ (25) | 603 |
| | $HO_2C(CH_2)_8CH=CH_2$ | Peroxide | $HO_2C(CH_2)_{10}Si(C_6H_5)_3$ (96) | 606 |
| | $n\text{-}C_{16}H_{31}CH=CH_2$ | Peroxide | $n\text{-}C_{18}H_{35}Si(C_6H_5)_3$ (46) | 291 |
| | $C_2H_5O_2C(CH_2)_8CH=CH_2$ | Peroxide | $C_2H_5O_2C(CH_2)_{10}Si(C_6H_5)_3$ | 606 |
| | $n\text{-}C_{12}H_{25}CH=CH_2$ | Peroxide | $n\text{-}C_{14}H_{29}Si(C_6H_5)_3$ (52) | 291 |
| | $n\text{-}C_{14}H_{29}CH=CH_2$ | Peroxide | $n\text{-}C_{16}H_{33}Si(C_6H_5)_3$ (45) | 291 |
| | $n\text{-}C_{16}H_{33}CH=CH_2$ | Peroxide | $n\text{-}C_{18}H_{37}Si(C_6H_5)_3$ (40) | 291 |
| | $(C_6H_5)_3SiCH_2CH=CH_2$ | Peroxide | $(C_6H_5)_3Si(CH_2)_3Si(C_6H_5)_3$ (36) | 293, 312 |

### D. Silanes and Acetylenes

| Silane | Acetylene | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $Cl_3SiH$ | $HC\equiv CH$ | Peroxide | $Cl_3Si(CH_2)_2SiCl_3$ (3) | 257, 607 |
| | | Hot tube | $Cl_3SiCH=CH_2$ (—) | 295 |
| | $n\text{-}C_3H_7C\equiv CH$ | Peroxide | $n\text{-}C_3H_7CH=CHSiCl_3$ (38) | 283, 285 |
| | | Peroxide | $n\text{-}C_3H_7CH=CHSiCl_3$ (20) | 282 |
| | | Thermal | $n\text{-}C_3H_7CH=CHSiCl_3$ (—) | 682 |
| | | UV | $n\text{-}C_3H_7CH=CHSiCl_3$ (—) | 582 |
| | $i\text{-}C_3H_7C\equiv CH$ | Peroxide | $i\text{-}C_3H_7CH=CHSiCl_3$ (37) | 285 |
| | $n\text{-}C_4H_9C\equiv CH$ | Thermal | $n\text{-}C_4H_9CH=CHSiCl_3$ (15) | 608 |
| | | Peroxide | $n\text{-}C_4H_9CH=CHSiCl_3$ (30) | 283, 285 |
| | $t\text{-}C_4H_9C\equiv CH$ | Peroxide | $t\text{-}C_4H_9CH=CHSiCl_3$ (39) | 285 |
| | $(CH_3)_3SiC\equiv CCH_3$ | Peroxide | $(CH_3)_3SiC(SiCl_3)=CHCH_3$ (—) | 284 |
| | $n\text{-}C_5H_{11}C\equiv CH$ | Peroxide | $n\text{-}C_5H_{11}CH=CHSiCl_3$ (47) | 283, 285 |

| | | | |
|---|---|---|---|
| $CH_3OCH=CH_2$ | UV | $CH_3OCH_2CH_2PH_2$ (—)<br>$[CH_2OCH_2CH_2]_2PH$ (—)<br>$(CH_2OCH_2CH_2)_3P$ (—) | 316, 615 |
| $CH_2=CUCH_2OH$ | UV | $HOCH_2CH_2CH_2PH_2$ (26)<br>$[HOCH_2CH_2CH_2]_2PH$ (5) | 316, 317, 615 |
|  | UV | $[HOCH_2CH_2CH_2]_3P$ (3) | 316, 317, 615 |
| $CH_2=CHCH_2NH_2$ | UV | $H_2NCH_2CH_2CH_2PH_2$ (38)<br>$(H_2NCH_2CH_2CH_2)_2PH$ (20) | 316, 317, 615 |
|  |  | $(H_2NCH_2CH_2CH_2)_3P$ (—) | 331 |
|  |  | $[H_2NCH_2CH_2CH_2]_3P$ (—) | 316, 613 |
| $C_3H_7CH=CH_2$ | None added | $CH_3(CH_2)_4PH_2$ (6) | 331 |
|  | UV | $CH_3(CH_2)_4PH$ [28–67] | 316, 317, 615 |
| $CH_2CH=CHCH_3$ | UV or peroxide | $CH_3(CH_2)_4PH$ (6)<br>$C_4H_9PH$ (2) | 316, 615 |
| $(CH_3)_2O_2CH=CH_2$ | Peroxide | $CH_3C(CH_3)_2CH_2PH_2$ (—)<br>$C_4H_9PH$ (2) | 318, 615 |
| $C_6H_5O_2CH=CH_2$ | Acetonitrile | $C_6H_5(CH_2CH_2)_2PH$ (18–24)<br>$(CH_2CH_2)_2P$ (7–11)<br>$[C_6H_5(CH_2CH_2)_2P$ (33–52)<br>$(C_6H_5O_2CH_2CH_2)_3P$ (21) | 318, 615, 316 |
|  |  | $(C_6H_5O_2CH_2CH_2)_2PH$ (115–20)<br>$C_6H_5O_2CH_2CH_2PH_2$ (24)<br>$[C_6H_5O_2CH_2CH_2]_2P$<br>$CHCO_2C_6H_5(CH_2PH)O_2C_6H_5$ (9–19) | 318 |
| (cyclohexene structure) | Acetonitrile or UV | $PH_3$ (49) | 318, 316 |
|  | Acetonitrile or UV | $PH$ (23) | 317, 615 |
| $n$-$C_4H_7OCH=CH_2$ | Acetonitrile | $n$-$C_4H_9OCH_2CH_2PH$ (45)<br>$[n$-$C_4H_9OCH_2CH_2]_2PH$ (20)<br>$(n$-$C_4H_9OCH_2CH_2)_2P$ (10) | 318 |
| $C_2H_5OCH_2CH=CH_2$ | Acetonitrile | $C_2H_5OCH_2(CH_2)_2PH_2$ (38)<br>$[C_2H_5OCH_2(CH_2)_2]PH$ (29)<br>$(C_2H_5OCH_2(CH_2)_2)_3P$ (6) | 318 |

*Note:* References 385 to 631 are on pp 371–376.

## TABLE XIII

### FORMATION OF PHOSPHORUS-CARBON BONDS

#### A. Phosphorus Trichloride

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $PCl_3$ | $CH_2{=}CHC_2H_5 + O_2$ | | $\left.\begin{array}{l}C_2H_5CHClCH_2POCl_2 \\ C_2H_5CH(CH_2Cl)POCl_2\end{array}\right\}$ (7.5) | 341 |
| | $CH_3CH{=}CHCH_3 + O_2$ | | $CH_3CHClCH(CH_3)POCl_2$ (20) $CH_3CHClCH(CH_3)POCl_2$ (31) | 341 |
| | cyclohexene $+ O_2$ | | $\left.\begin{array}{l}C_6H_{10}ClPOCl_2 \\ C_6H_9POCl_2\end{array}\right\}$ (40) | 341 |
| | cyclohexenyl $CH{=}CH_2$ | UV | $CHClCH_2PCl_2$ (17) | 611 |
| | $CH_2{=}CHC_6H_{13}{-}n$ | Peroxide | $n{-}C_6H_{13}CHClCH_2PCl_2$ (33) | 340, 612–614 |

#### B. Phosphines

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $PH_3$ | $CFCl{=}CF_2$ | None added | $CHFClCF_2PH_2$ (54) $(CHFClCF_2)_2PH$ (6) $H_2PCFClCF_2PH_2$ (1) | 331 |
| | $CCl_2{=}CF_2$ | None added | $CHCl_2CF_2PH_2$ (30) $(CHCl_2CF_2)_2PH$ (3) $H_2PCCl_2CF_2PH_2$ (53) | 331 |
| | $CF_2{=}CF_2$ | None added | $CHF_2CF_2PH_2$ (53) $(CHF_2CF_2)_2PH$ (7) $H_2PCF_2CF_2PH_2$ (8) | 331 |
| | $CF_2{=}CH_2$ | None added | $CHF_2CH_2PH_2$ (1) | 331 |
| | $CF_3CF{=}CF_2$ | None added | $CF_3CF(PH_2)CF_2H$ (36) | 331 |
| | $CH_2ClCH{=}CH_2$ | UV | $CH_2ClCH_2CH_2PH_2$ (—) $(CH_2ClCH_2CH_2)_2PH$ (—) $(CH_2ClCH_2CH_2)_3P +$ phosphorus-containing polymer | 316, 317, 615 |

| | | | |
|---|---|---|---|
| $HC\equiv CC_4H_9$-n | | Azonitrile | 318 |
| $CH_2=CHCO_2C_2H_5$ | | Azonitrile | 318 |
| $CH_2=C(CH_3)CO_2CH_3$ | | Azonitrile | 318 |
| $CH_2=CHOCOCH_3, CH_2=CHC_4H_9$-n | | Azonitrile | 318 |

$(NCCH_2CH_2CH_2)_3P$, $(NCCH_2CH_2)_2PH=CHC_3H_6$-n, $n$-(39)
$(NCCH_2CH_2)_2PCH_2CH_2CH(CH_3)CH_2C(CH_3)_2$, $n$-(38)
$(NCCH_2CH_2)_2PC_2H_5$
$OC(CH_3)_2CH_2P(CH_2CH_2CN)_2$, $n$-(31)
$[n$-$C_4H_9CH(CO_2C_2H_5)CH_2]_3P$, $n$-(31)
$2$ $l$ $adduct$ $(?)$

| $C_6H_5O_2CCH(CH_3)CH_2P_3H$ | | Azonitrile | 318 |
| | $C_6H_5O_2CCH(CH_3)CH_2CO_2C_2H_5P$ | | |
| | $[CH_2CO_2C_2H_4]_2$ (76) | | |

$(n\text{-}C_3H_7)_3PH$

| $(CH_3)_3P$ | | | |
| | $(CH_3)_2CH$ $P$ $CHCH_3$ | Azonitrile | 318 |
| | $CH(CH_3)_2$ | | |

| $C_2H_5O_2CC$ $CHCH_3$ | | | |
| | $(CH_3)_2CH$ $P$ $CHCH_3$ | (55) | |
| | $CH(CH_3)_2$ | | |

$H_2P(O)OH$

**C. Hypophosphorous Acid and Salts**

| | | | |
|---|---|---|---|
| $CH_2=CHC_4H_9$-n | | $C_4H_9P(O)OH$ (9) | Peroxide | 320 |
| | | $n$-$C_4H_9P(O)OH$ (9) | | |
| $CH_2=CHC_4H_9$-n | | $HOPH(O)C_4H_8CO_2C_4H_9$-n (65) | None added | 617 |

| $CH_2=CHC_6H_5$ | | | | |
| $CH_3CO_2C_6H_5$ | | $C_8H_{17}CO_2C_2H_5$ | | |
| | | | Peroxide | 126 |
| $CH_2=CHC_6H_{13}$-n | | $(n\text{-}C_8H_{17})P(O)OH$ (22) | Peroxide | 126 |
| $CH_2=CHC_7H_{15}$-n | | $(n\text{-}C_8H_{17})P(O)OH$ (19) | Peroxide | 225 |
| $CH_2=C(C_3H_7)_2CH_3$ | | $(n\text{-}C_8H_{17})P(O)OH$ (14) | Peroxide | 225 |

| $CH_2=CHC_6H_{13}$-n | | $HOPH(O)C_8H_{16}CO_2C_8H_{17}$-n (63) | None added | 617 |

$CH_3CO_2C_6H_{11}$

| $CH_2=CHCH_2OH$ | | $(n\text{-}C_3H_7)_3P(O)OH$ (17) | Peroxide | 326 |
| $CH_2=CHC_6H_{13}$-n | | $(n\text{-}C_8H_{17})_3P(O)OH$ (25) | Peroxide | 126 |
| $CH_2=CHC_8H_{17}$-n | | $(n\text{-}C_{10}H_{21})_3P(O)OH$ (40) | Peroxide | 326 |

## TABLE XIII—Continued

### B. Phosphines—Continued

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $PH_3$ (contd.) | $CH_2{=}CHC_6H_{13}{\text-}n$ | Azonitrile | $n{\text-}C_8H_{17}PH_2$ (0–75)<br>$(n{\text-}C_8H_{17})_2PH$ (0–38)<br>$(n{\text-}C_8H_{17})_3P$ (4–100) | 316, 316, 616, 615 |
| | $CH_2{=}CHC_{10}H_{21}{\text-}n$ | Azonitrile | $n{\text-}C_{12}H_{25}PH_2$ (23)<br>$(n{\text-}C_{12}H_{25})_2PH$ (20)<br>$(n{\text-}C_{12}H_{25})_3P$ (26) | 318 |
| **Monosubstituted Phosphines** | | | | |
| $NCCH_2CH_2PH_2$ | $CH_2{=}CHCH_2OH$ | X-ray or azonitrile | $NCCH_2CH_2PH(CH_2)_3OH$ (31)<br>$NCCH_2CH_2P[(CH_2)_3OH]_2$ (17) | 318 |
| | $CH_2{=}CHCH_2NH_2$ | X-ray | $NCCH_2CH_2PH(CH_2)_3NH_2$ (18)<br>$NCCH_2CH_2P[(CH_2)_3NH_2]_2$ (56) | 318 |
| | (cyclohexene) | Peroxido | (cyclohexyl)$PHCH_2CH_2CN$ (65) | 318 |
| | $(CH_3)_2C{=}CHCOCH_3$ | Azonitrile | $NCCH_2CH_2PHC(CH_3)_2CH_2COCH_3$ (8) | 318 |
| | $HC{\equiv}CC_5H_{11}{\text-}n$ | Azonitrile | $NCCH_2CH_2P(CH{=}CHC_6H_{11}{\text-}n)_2$ (20) | 318 |
| | $CH_2{=}CHC_6H_{13}{\text-}n$ | Peroxido or azonitrile | $NCCH_2CH_2PHC_8H_{17}{\text-}n$ (0–39)<br>$NCCH_2CH_2P(C_8H_{17}{\text-}n)_2$ (25–93) | 318 |
| $C_2H_5O_2CCH_2CH_2PH_2$ | $CH_2{=}CHC_6H_{13}{\text-}n$ | Peroxido | $C_2H_5O_2CCH_2CH_2PHC_8H_{17}{\text-}n$ (31)<br>$C_2H_5O_2CCH_2CH_2P(C_8H_{17}{\text-}n)_2$ (60) | 318 |
| $C_6H_5PH_2$ | $CH_2{=}CHCH_2OH$ | Azonitrile | $C_6H_5P(CH_2CH_2CH_2OH)_2$ (56) | 319 |
| **Disubstituted Phosphines** | | | | |
| $(NCCH_2CH_2)_2PH$ | $CH_2{=}CHCN$ | Azonitrile | $(NCCH_2CH_2)_3P$ (02) | 318 |
| | $CH_2{=}CHCH_2OH$ | X-ray or peroxido | $(NCCH_2CH_2)_2P(CH_2)_3OH$ (78) | 318 |
| | (cyclohexene) | Azonitrile | (cyclohexyl)$P(CH_2CH_2CN)_2$ (55) | 318 |
| | $HC{\equiv}CC_5H_{11}{\text-}n$ | Azonitrile | $(NCCH_2CH_2)_2PCH{=}CHC_6H_{11}{\text-}n$ (27) | 318 |
| | $C_6H_5CH{=}CH_2$ | Poroxido | $(NCCH_2CH_2)_2PCH_2CH_2C_6H_5$ (47) | 318 |

| | | | |
|---|---|---|---|
| CH₂=CHC₉H₁₉ | Peroxide | n-C₅H₁₁PO(OH)₂, (18) | 120 |
| CHCO₂C₂H₅<br>‖<br>CHCO₂C₂H₅ | None added | (HO)₂PO(CH)C₆H₅·CH₂PO(OH)₂, (18) | 017 |
| CHCO₂C₂H₅<br>‖<br>CHCO₂C₂H₅ | None added | (HO)₂PO(CH)₂C₆H₅, (7) | 617 |
| **HPO(OCH₃)₂** | | | |
| C₆H₅CH=CH₂ | Peroxide | C₆H₅CO₂CH₂CH₂PO(OCH₃)₂ (61) | 314 |
| n-C₆H₁₃CH=CH₂ | Peroxide | n-C₈H₁₇PO(OCH₃)₂ (65) | 334 |
| CH₂=CHPO(OCH₃)₂ | UV or peroxide | C₂H₄[PO(OCH₃)₂]₂ (55) | 437 |
| CH₂=CHSi(OC₂H₅)₃ | Acetone | (C₂H₅O)₃SiCH₂CH₂PO(OCH₃)₂ (31) | 618, 629 |
| CH₂=CHC₄H₉ | UV or peroxide | n-C₇H₁₅PO(OCH₃)₂ (56) | 337 |
| CH₂=CH—CH₂—CH₃ | UV or peroxide | n-C₆H₁₃PO(OCH₃)₂ (62) | 337 |
| CH₂=CH—CH₂—C₂H₅ | UV or peroxide | n-C₇H₁₅PO(OCH₃)₂ (61) | 337 |
| CH₂=CH—CH₂—C₄H₉ | UV or peroxide | n-C₉H₁₉PO(OCH₃)₂ (45) | 337 |
| CH₂=CH—CO₂CH₃ | UV or peroxide | (CH₃O)₂PO(CH₂)₂CO₂CH₃ (60) | 337 |
| CH₂=CHC₆H₁₃ | Peroxide | n-C₉H₁₉PO(OCH₃)₂ (51) | 334 |
| CH₂=CHCO₂CH₃ | Peroxide or UV | | 124 |
| n-C₆H₁₃CH=CH₂ | Peroxide or UV | n-C₁₂H₂₅PO(OCH₃)₂ (49) | 334 |
| CH₂(CH₂)₁₀CH=CH—CH₂PO(OCH₃)₂ | Peroxide | CH₂(CH₂)₁₀CHPO(OCH₃)₂ (69)<br>(CH₂)₁₀CO₂CH₃ | 334 |
| **HPO(OC₂H₅)₂** | | | |
| n-C₇H₁₅CH=CH₂ | Peroxide or acetanilide | n-C₉H₁₉CH₂CH₂CH₂PO(OC₂H₅)₂ (42) | 324 |
| CF₂=CF₂<br>(400 p.s.i.) | Peroxide | HCF₂CF₂PO(OC₂H₅)₂ (—)<br>(aₚ = λ-4)<br>+ higher telomers | 325 |
| C₅H₁₁CH=CH₂ | Peroxide | C₄H₉PO(OC₂H₅)₂,CH₂CH₂PO(OC₂H₅)₂ (14) | 335 |
| CH₂=CHCH₂CH=CH₂ | Peroxide | CH₃CO₂CH₂CH₂CH₂PO(OC₂H₅)₂ (—)<br>+ phosphorus-containing residue | 338 |
| CH₃CO₂CH₂CH=CH₂ | | CH₃CO₂CH₂CH₂CH₂OCO₂CH₂CH₂<br>PO(OC₂H₅)₂ (—) | 621 |

## TABLE XIII—Continued

### C. Hypophosphorous Acid and Salts—Continued

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $H_2P(O)ONa$ | $CH_2{=}C(CH_3)CH_2OH$ | Peroxide | $HOCH_2CH(CH_3)CH_2PH(O)ONa$ (—) | 332 |
| | $CH_2{=}CH(CH_2)_2OH$ | Peroxide | $HO(CH_2)_4PH(O)ONa$ (—) | 332 |
| | $CH_2{=}CHC_4H_9\text{-}n$ | Peroxide | $n\text{-}C_6H_{13}PH(O)ONa$ (100) | 327, 328 |
| | $CH_2{=}CHC_6H_{13}\text{-}n$ | Peroxide | $n\text{-}C_8H_{17}PH(O)ONa$ (100) | 327, 328, 618 |
| | $CH_2{=}CHC_{12}H_{25}\text{-}n$ | Peroxide | $n\text{-}C_{14}H_{29}PH(O)ONa$ (80) | 327, 328, 618 |

### D. Phosphorous Acid and Esters
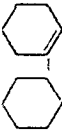
| | | | | |
|---|---|---|---|---|
| $HPO(OH)_2$ |  | Peroxide |  $PO(OH)_2$ (20) <br>  (9) $PO(OH)_2$ | 320, 321 |
| | $CH_2{=}CHC_4H_9\text{-}n$ | Peroxide | $n\text{-}C_6H_{13}PO(OH)_2$ (23) <br> $n\text{-}C_6H_{13}CH(C_4H_9\text{-}n)CH_2PO(OH)_2$ (8) | 320 |
| | $\begin{array}{c}CHCO_2C_2H_5 \\ \| \\ CHCO_2C_2H_5\end{array}$ | None added | $(HO)_2P(O)CHCO_2C_2H_5$ (16) <br>    &#124; <br> $CH_2CO_2C_2H_5$ | 617 |
| | $CH_2{=}CHC_6H_{13}\text{-}n$ | Peroxide or UV | $n\text{-}C_8H_{17}PO(OH)_2$ (18–28) <br> $n\text{-}C_8H_{17}CH(C_6H_{13}\text{-}n)CH_2PO(OH)_2$ (—) <br> + high mol. wt. oil | 321 |
| |  | Peroxide or UV |  $PO(OH)_2$ (18–23) <br> + high mol.-wt. oil | 321 |

| | | | |
|---|---|---|---|
| (cyclohexane) CH₂CH₂Si(CH₃)₂OC₂H₅)₄ | Peroxide | (C₇H₁₅)₂Si(CH₂CH₂CH₃)₄ ...PO(OC₂H₅)₃ (92) | 322 |
| HPO(OC₂H₅)₂ | Peroxide | C₆H₁₃CH(C₂H₅)PO(OC₂H₅)₂ (86) | 622, 621 |
| | Peroxide | n-C₇H₁₅CO₂CH₃ [CH₂PO(OC₂H₅)₂] (57) | 334 |
| | Peroxide | CH₃...PO(OC₂H₅)[CH₂]ₙ (—) | 330 |
| | Peroxide or UV | (C₄H₉O)₂PO(CH₂)ₙC₂H₅ | 334 |
| | | CH₃CH(CH₂)₁₀C₂H₅ (53) | |
| | Peroxide | n-C₁₀H₂₁CO₂CH₂PO(OC₄H₉)₂ (49) | 334 |
| | Peroxide | CH₃[CH₂CH(CH₂)ₙPO(OC₄H₉)₂] (—) | 334 |
| | | (CH₂)₁₀₋₁₂CO₂C₄H₉ (87) | |
| HPO(OC₄H₉-n)₂ | Peroxide | CH₃(CH₂)₇CH=CH(CH₂)₇CO₂H₃[CH₂]₂CO₂... (88) | 220 |
| | | | 234 |
| | Peroxide | = C₆H₅CH(C₂H₅)CH₂PO₃O | 234 |
| (cyclohexane) | | | 334 |
| HOCH₂CH₂—CH₃ | Peroxide | HO(CH₂)₂PO(OC₂H₅)₂ (30) | 327, 328 |
| HOCH₂CH₂—CH₃ | UV or peroxide | C₄H₉PO(OC₂H₅)₃ (nₓ) (69) | 337 |
| HO(CH₂)₂—CHCH₂ | Peroxide | HO(CH₂)₂CH₂PO(OC₂H₅)₂ (nₓ) | 327, 328 |
| CH₃CH—CHCH₂ | Peroxide | CH₃CH₂CH₂PO(OC₂H₅)ₙ (77) | 324 |
| C₄H₉CO₂CH—CH₂ | Peroxide | C₄H₉CO₂CH₂PO(OC₄H₉)₂ (45) | 334 |
| (CH₃)₂SiCH—CH₂ | Peroxide | C₄H₉CH₂CH₂PO(OC₄H₉)₂ (55) | 334 |
| (cyclohexane) | Peroxide | PO(OC₂H₅)ₙ (nₓ) (32) | 322 |
| (CH₂—CHCH₂)₂O | | = C₆H₅CH(CH₂)ₙ... | 327, 328, 324 |
| C₂H₅CO₂CH—CH₂ | Peroxide | [n-C₆H₁₃CH₂PO(OC₂H₅)₂] (28) | 327, 328 |
| CH₃CH—CH₂CO₂C₄H₉ | Peroxide | CH₃CH(CH₂)₂CH₂PO(OC₄H₅-n)₂ (68) | 337 |
| | Peroxide | n-C₆H₁₃CO₂C₂H₅PO(OC₂H₅-n)₂ (58) | 334 |
| n-C₇H₁₅CH=CH₂ | UV or peroxide | n-C₆H₁₃CH(PO(OC₄H₉)₂)CH₂PO(OC₄H₉)₂ (30) | 327, 323 |
| | | (n-C₄H₉O)₂POCH(CH₃)CH₂CH₂C₄H₉ (55) | 327, 618, 327, 324, 324 |
| | | + higher telomers (19) | |

## TABLE XIII—Continued

### D. Phosphorous Acid and Esters—Continued

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $HPO(OC_2H_5)_2$ (contd.) | $CH_3CO_2C(CH_3)=CH_2$ | Peroxide | $CH_3CO_2CH(CH_3)CH_2PO(OC_2H_5)_2$ (72) + higher telomers (10) | 333 |
| | $C_2H_5CO_2CH=CH_2$ | Peroxide | $C_2H_5CO_2CH_2CH_2PO(OC_2H_5)_2$ (55) | 334 |
| | (cyclohexene ring) | UV | (ring)$PO(OC_2H_5)_2$ (—) + polymer | 337 |
| | $n\text{-}C_3H_7CO_2CH=CH_2$ | Peroxide | $n\text{-}C_3H_7CO_2CH_2CH_2PO(OC_2H_5)_2$ (45) | 334 |
| | $n\text{-}C_4H_9CH=CH_2$ | UV or peroxide | $n\text{-}C_6H_{13}PO(OC_2H_5)_2$ (29) | 327, 328, 324, 337 |
| | | UV | $n\text{-}C_4H_9CH(CH_3)_2CH_2PO(OC_2H_5)_2$ (18) | 337 |
| | $n\text{-}C_3H_7CH=CHCH_3$ | Peroxide | $n\text{-}C_4H_9CH(CH_3)CH_2PO(OC_2H_5)_2$ (29) | 322 |
| | $C_2H_5OSi(CH_3)_2CH=CH_2$ | UV | $C_2H_5OSi(CH_3)_2CH_2CH_2PO(OC_2H_5)_2$ (55) | 337 |
| | $n\text{-}C_4H_9CH=CHCH_3$ | Peroxide | $n\text{-}C_6H_{13}CH(CH_3)PO(OC_2H_5)_2$ (30) | 322 |
| | $C_2H_5OSi(CH_3)_2CH_2CH=CH_2$ | Azonitrile or peroxide | $C_2H_5OSi(CH_3)_2CH_2CH_2CH_2PO(OC_2H_5)_2$ (62) | 619, 322, 620 |
| | $(C_2H_5O)_3Si(CH_2)_3CH=CH_2$ | | $(C_2H_5O)_3Si(CH_2)_3CH_2CH_2PO(OC_2H_5)_2$ (37–46) | |
| | $n\text{-}C_6H_{13}CH=CH_2$ | Peroxide, azonitrile, or UV | $n\text{-}C_6H_{13}CH_2PO(OC_2H_5)_2$ (43–60) | 323, 337, 621 |
| | | Peroxide, aro-nitrile, or UV | $C_{10}H_{23}PO(OC_2H_5)_2$ (3–25) | |
| | $(C_2H_5O)_3SiCH_2CH=CH_2$ | Peroxide | $(C_2H_5O)_3SiCH_2CH_2CH_2PO(OC_2H_5)_2$ (33) | 322 |
| | $n\text{-}C_7H_{15}CH=CH_2$ | UV or peroxide | $n\text{-}C_7H_{15}PO(OC_2H_5)_2$ (50) | 337 |
| | $n\text{-}C_8H_{17}CH=CH_2$ | UV or peroxide | $n\text{-}C_{10}H_{21}PO(OC_2H_5)_2$ (37) | 337 |
| | $n\text{-}C_8H_{17}CO_2CH=CH_2$ | Peroxide | $n\text{-}C_8H_{17}CO_2CH_2CH_2PO(OC_2H_5)_2$ (50) | 334 |
| | (cyclohexene ring) | Peroxide | (ring) (—) | 320 |
| | (cyclohexane ring) | | (ring)$PO(OC_2H_5)_2$ | |
| | $n\text{-}C_{10}H_{21}CH=CH_2$ | Peroxide | $n\text{-}C_{12}H_{25}PO(OC_2H_5)_2$ (86) | 621 |
| | $n\text{-}C_9H_{19}C(C_2H_5-n)=CH_2$ | Peroxide | $n\text{-}C_9H_{19}C(C_2H_5-n)CH_2PO(OC_2H_5)_2$ (—) | 320 |
| | $CH_2=CH(CH_2)_8CO_2C_2H_5$ | Peroxide or UV | $(C_2H_5O)_2P(O)(CH_2)_{10}CO_2C_2H_5$ (58) | 334 |

| Refs |
|---|
| 334 |
| 334 |

| Peroxide |
|---|
| Peroxide |

n $C_9H_{19}CO_2CH_2CH_2PO$
[$OCH_2CH_2C_6H_4C_6H_4$-n]₂ (46)

$CH_3(CH_2)_3CH=CH(CH_2)_3$
[$PO(OCH_2CH(C_2H_5)C_4H_9$-n)₂ CH₂]₂

n-$C_6H_4CH(C_6H_5)CH_2OCO$ (67)

### E. Esters of Thiophosphorous Acid

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs |
|---|---|---|---|---|
| HPS(OC₄H₉-n)₂ | (cyclohexene) | UV or peroxide | PS(OC₄H₉)₃ (61) | 339 |
| | n C₂H₅CH=CH₂ | UV or peroxide | n-C₄H₉PS(OC₄H₉)₂ (60) | 339 |
| | n C₄H₉CH=CH₂ | UV or peroxide | n-C₆H₁₃PS(OC₄H₉)₂ (60) | 339 |
| | n C₆H₁₃CH=CH₂ | UV or peroxide | n-C₈H₁₇PS(OC₄H₉)₂ (30) | 339 |
| | n C₈H₁₇CH=CH₂ | UV or peroxide | n-C₁₀H₂₁PS(OC₄H₉)₂ (54) | 339 |
| | n C₉H₁₉CH=CH₂ | UV or peroxide | n-C₁₁H₂₃PS(OC₄H₉)₂ (60) | 339 |
| HPS(OC₄H₉-n)₂ | (cyclohexene) | UV or peroxide | PS(OC₄H₉)₃ (44) | 339 |
| | n C₂H₅CH=CH₂ | UV or peroxide | n-C₄H₉PS(OC₄H₉-n)₂ (43) | 339 |
| | n C₄H₉CH=CH₂ | UV or peroxide | n-C₆H₁₃PS(OC₄H₉-n)₂ (38) | 339 |
| | n C₆H₁₃CH=CH₂ | UV or peroxide | n-C₈H₁₇PS(OC₄H₉-n)₂ (40) | 339 |
| | n C₈H₁₇CH=CH₂ | UV or peroxide | n-C₁₀H₂₁PS(OC₄H₉-n)₂ (41) | 339 |
| | n C₉H₁₉CH=CH₂ | UV or peroxide | n-C₁₁H₂₃PS(OC₄H₉-n)₂ (72) | 339 |
| HPS(OC₅H₁₁-n)₂ | (cyclohexene) | UV or peroxide | PS(OC₅H₁₁-n)₃ (58) | 339 |
| | n C₂H₅CH=CH₂ | UV or peroxide | n-C₄H₉PS(OC₅H₁₁-n)₂ (33) | 339 |
| | n C₄H₉CH=CH₂ | UV or peroxide | n-C₆H₁₃PS(OC₅H₁₁-n)₂ (46) | 339 |
| | n C₆H₁₃CH=CH₂ | UV or peroxide | n-C₈H₁₇PS(OC₅H₁₁-n)₂ (56) | 339 |

*Note. References 283 to 421 are on pp. 371–376.*

## TABLE XIII—Continued

### D. Phosphorous Acid and Esters—Continued

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $HPO(OC_4H_9\text{-}n)_2$ (contd.) | $(CH_3)_2CCH_2C(CH_3)=CH_2$ | Peroxide | $(CH_3)_2CCH_2CH(CH_3)CH_2CH_2PO(OC_4H_9\text{-}n)_2$ (42) | 324 |
| | $n\text{-}C_4H_9OSi(CH_3)_2CH=CH_2$ | Peroxide | $n\text{-}C_4H_9OSi(CH_3)_2CH_2CH_2PO(OC_4H_9\text{-}n)_2$ (59) | 322 |
| | $(C_2H_5O)_3SiCH=CH_2$ | Azonitrile | $(C_2H_5O)_3SiCH_2CH_2PO(OC_4H_9\text{-}n)_2$ (37) | 619, 620 |
| | $n\text{-}C_8H_{17}CH=CH_2$ | Peroxide | $n\text{-}C_{10}H_{21}PO(OC_4H_9\text{-}n)_2$ (25) | 328, 327, 324 |
| | | | $n\text{-}C_{10}H_{21}CH(C_8H_{17}\text{-}n)CH_2PO(OC_4H_9\text{-}n)_2$ (25) | |
| | $n\text{-}C_9H_{17}CO_2CH=CH_2$ | Peroxide | $n\text{-}C_9H_{17}CO_2CH_2CH_2PO(OC_4H_9\text{-}n)_2$ (45) | 334 |
| | $CH_2=CH(CH_2)_8CO_2C_4H_9\text{-}n$ | UV or peroxide | $(n\text{-}C_4H_9O)_2P(O)(CH_2)_{10}CO_2C_4H_9\text{-}n$ (66) | 334 |
| | $n\text{-}C_3H_7CO_2CH=CH_2$ | Peroxide | $n\text{-}C_3H_7CO_2CH_2CH_2PO(OC_4H_9\text{-}n)_2$ (60) | 334 |
| | $n\text{-}C_{17}H_{35}CO_2CH=CH_2$ | Peroxide | $n\text{-}C_{17}H_{35}CO_2CH_2CH_2PO(OC_4H_9\text{-}n)_2$ (47) | 334 |
| | $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$ | Peroxide | $CH_3(CH_2)_{7(6)}CH[PO(OC_4H_9\text{-}n)_2](CH_2)_{8(7)}$ (77) <br> $\quad\quad\quad\quad \mid$ <br> $\quad\quad\quad C_2H_5OCO$ | 334 |
| | $CH_3(CH_2)_7CH=CH(CH_2)_7\text{-}$<br>$CO_2C_4H_9\text{-}n$ | Peroxide | $CH_3(CH_2)_{7(6)}CH[PO(OC_4H_9\text{-}n)_2][(CH_2)_{8(7)}$ (66) <br> $\quad\quad\quad\quad \mid$ <br> $\quad\quad\quad n\text{-}C_4H_9OCO$ | 334 |
| $HPO[OCH_2CH(C_2H_5)C_4H_9\text{-}n]_2$ | $C_2H_5CO_2CH=CH_2$ | Peroxide | $C_2H_5CO_2(CH_2)_2PO[OCH_2CH(C_2H_5)\cdot$<br>$C_4H_9\text{-}n]_2$ (45) | 334 |
| | $n\text{-}C_3H_7CO_2CH=CH_2$ | Peroxide | $n\text{-}C_3H_7CO_2CH_2CH_2PO\text{-}$<br>$[OCH_2CH(C_2H_5)C_4H_9\text{-}n]_2$ (52) | 334 |
| | $n\text{-}C_8H_{17}CO_2CH=CH_2$ | Peroxide | $n\text{-}C_8H_{17}CO_2CH_2CH_2PO\text{-}$<br>$[OCH_2CH(C_2H_5)C_4H_9\text{-}n]_2$ (49) | 334 |
| | $CH_2=CH(CH_2)_8CO_2C_2H_5$ | UV or peroxide | $[n\text{-}C_4H_9CH(C_2H_5)CH_2O]_2\text{-}$<br>$P(O)(CH_2)_{10}CO_2C_2H_5$ (53) | 334 |
| | $n\text{-}C_{13}H_{27}CO_2CH=CH_2$ | Peroxide | $n\text{-}C_{13}H_{27}CO_2CH_2CH_2PO\text{-}$<br>$[OCH_2CH(C_2H_5)C_4H_9\text{-}n]_2$ (49) | 334 |
| | $CH_2=CH(CH_2)_{16}CO_2CH_2\text{-}$<br>$CH(C_2H_5)C_4H_9\text{-}n$ | UV or peroxide | $[n\text{-}C_4H_9CH(C_2H_5CH_2O)_2CH_2O]_2P(O)[CH_2]_{10}$ (61) <br> $\quad\quad\quad\quad\quad \mid$ <br> $\quad\quad\quad n\text{-}C_4H_9CH(C_2H_5)CH_2OCO$ | 334 |

## TABLE XIV

### Formation of Carbon-Nitrogen Bonds

(This table includes only reactions reported since 1945   See p 225 )

#### A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes

| Olefin | Conditions | Product (%) | Refs. |
|---|---|---|---|
| $CF_2=CCl_2$ | 65°/6 hr. | $O_2NCF_2CCl_2NO_2$ (47) | 365 |
| $CF_2=CFCl$ | 65°/6 hr. | $O_2NCF_2CFClNO_2$ (51) | 365 |
| $CF_2=CF_2$ | 65°/6 hr. | $O_2NCF_2CF_2NO_2$ (53) | 365, 364 |
| $CH_2=CF_2$ | $CCl_4$/press /40-60° | $O_2NCH_2CF_2NO_2$ | 623 |
| | | $O_2NCH_2CF_2OH$* | |
| $CH_2=CH_2$ | Ether/8 hr./0° | $O_2NCH_2CH_2NO_2$ | 352 |
| | | $O_2NCH_2CH_2OH$* (35-40) | |
| | | $O_2NCH_2CH_2OH$* (12-20) | |
| $CH_3CH=CH_2$ | | $O_2NCH_2CH(CH_3)NO_2$ (12-20) | 368 |
| | | Explosive reaction on removal of solvent. | 352 |
| | | $CH_3CH(NO_2)CH_2NO_2$ (25-30) | |
| | | $CH_3CH(OH)CH_2NO_2$ (45-40) | |
| | | $CH_3CH(ONO_2)CH_2NO_2$ (2-20) | |
| $HC≡C-C≡CH$ | Ether | Violent reaction | 368 |
| | | $CH_3NO_2C=C(NO_2)CH_3$ (35) | 368 |
| | | $CH_3NO_2C=C(NO_2)CH_3$ trans (34)    cis (7) | 369 |
| $CH_2=CHCH=CH_2$ | Ether | $O_2NCH_2CH=CHCH_2NO_2$ (14) | 624 |
| $CH_2=CHCOOCH_3$ | | $O_2NCH_2CHCOOCH_3$ (27)† | 356 |
| | | $O_2NCH_2·CHCO_2CH_3$ (13)† | |
| | | ($CO_2H)_2$, 2H₂O (80)† | |
| $CH_3CH=CHCOOH$ | Ether | $CH_3CH(CH_3)CH(NO_2)CO_2H$ (51)* | 625 |

Note   References 365 to 631 are on pp 311-376
* The nitro alcohol is formed from the corresponding nitrite ester (CONO → COH) by hydrolysis, in working up the reaction mixture
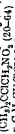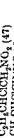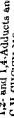† The unsaturated ester is presumed to come from $O_2NCH_2CH(ONO_2)CO_2CH_3$ and the oxalic acid from $O_2NCH_2CHOH·CO_2CH_3$

TABLE XIII—Continued

F. Phosphonic Acid Derivatives

| Phosphorus Compound | Unsaturate | Catalyst | Product (%) | Refs. |
|---|---|---|---|---|
| $C_2H_5PH(O)OCH_3$ | ⬡ (cyclohexene) | UV or peroxide | $P(C_2H_5)(O)OCH_3$ (40) | 339 |
| $C_2H_5PH(O)OC_2H_5$ | ⬡ (cyclohexene) | UV or peroxide | $P(C_2H_5)(O)OC_2H_5$ (25) | 339 |
|  | $n\text{-}C_5H_{11}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_7H_{15}(C_2H_5)P(O)OC_2H_5$ (57) | 339 |
| $C_2H_5PH(O)OC_4H_9\text{-}n$ | $n\text{-}C_7H_{15}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_9H_{19}(C_2H_5)P(O)OC_2H_5$ (65) | 339 |
|  | $n\text{-}C_5H_{11}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_7H_{15}(C_2H_5)P(O)OC_4H_9\text{-}n$ (46) | 339 |
| $C_6H_5PH(O)OCH_3$ | $n\text{-}C_7H_{15}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_9H_{19}(C_6H_5)P(O)OCH_3$ (35) | 339 |
| $C_6H_5PH(O)OC_2H_5$ | ⬡ (cyclohexene) | UV or peroxide | $P(C_6H_5)(O)OC_2H_5$ (33) | 339 |
|  | $n\text{-}C_5H_{11}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_7H_{15}(C_6H_5)P(O)OC_2H_5$ (45) | 339 |
|  | $n\text{-}C_6H_{13}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_8H_{17}(C_6H_5)P(O)OC_2H_5$ (37) | 339, 328, 327 |
| $n\text{-}C_6H_{13}PH(O)ONa$ | $n\text{-}C_7H_{15}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_9H_{19}(C_6H_{13})P(O)OC_2H_5$ (60) | 339 |
|  | $n\text{-}C_8H_{17}CH{=}CH_2$ | UV or peroxide | $n\text{-}C_{10}H_{21}(C_6H_{13})P(O)OC_2H_5$ (71) | 339 |
|  | $n\text{-}C_9H_{19}CH{=}CH_2$ | Peroxide | $(n\text{-}C_6H_{13})_2P(O)ONa$ (60) | 327, 328 |
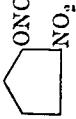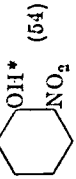
Note: References 385 to 631 are on pp. 371–376.

| Starting material | Conditions | Products | References |
|---|---|---|---|
| $(C_4H_9)_2C{=}CH_2$ | Olefin to $N_2O_4$ in ether | [cyclohexane ring] $ONO_2$ (2), $NO_2$; $NO_2$ (42), $NO_2$; $OH$ (25), $NO_2$; $ONO_2$ (19), $NO_2$ | 352, 376 |
|  | Olefin to $N_2O_4$ in ether | [ring] $ONO$, $NO_2$ (cis-trans ratio 42:48) (isolated as the nitro alcohol) | 358 |
|  | Ether/0° | $(C_2H_5)_2C(NO_3)CH_2NO_2$ (36); $(C_2H_5)_2C(OH)CH_2NO_2$* (41) | 627 |
| [cyclohexene with $CH_3$] | Olefin to $N_2O_4$ in ether | [ring] $CH_3$, $NO_2$, $ONO$ (trans only) (isolated as the nitro alcohol) | 338 |

Note   References 383 to 631 are on pp. 371–376.

\* The nitro alcohol is formed from the corresponding nitrate ester (CONO → COH) by hydrolysis, in working up the reaction mixture.

## TABLE XIV—Continued

### A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes—Continued

| Olefin | Conditions | Product (%) | Refs. |
|---|---|---|---|
| $CH_3C(NO_2)=C(NO_2)CH_3$ | 85°/75 hr. | $CH_3C(NO_2)_2C(NO_2)_2CH_3$ (31) | 366 |
| $C_2H_5CH=CH_2$ | Ether | $C_2H_5CH(NO_2)CH_2NO_2$ (39)<br>$C_2H_5CHOHCH_2NO_2$* (33) | 352, 353 |
| $CH_3CH=CHCH_3$ | Ether | $CH_3CH(NO_2)CH(NO_2)CH_3$ (30)<br>$CH_3CHOHCH(NO_2)CH_3$* (35) | 352, 353 |
| $(CH_3)_2C=CH_2$ | Ether | $(CH_3)_2C(NO_2)CH_2NO_2$ (35–42)<br>$(CH_3)_2COHCH_2NO_2$* (25–30)<br>$(CH_3)_2C(ONO)CH_2NO_2$ (2)<br>$O_2NCH_2C(CH_3)(OH)CH_2NO_2$ (5–9) | 352, 353 |
| (cyclopentene) |  | (ring) ONO / NO₂   (cis-trans ratio 16:84) | 358 |
| $(CH_3)_2C=CHCH_3$ | −60°/no solvent | $(CH_3)_2C(ONO_2)CH(NO_2)CH_3$ (42)<br>$(CH_3)_2C(OH)CH(NO_2)CH_3$* (58) | 626 |
| $C_2H_5C\equiv CC_2H_5$ |  | $C_2H_5(NO_2)C=C(NO_2)C_2H_5$ trans (31)<br>cis (5)<br>$C_2H_5COC(NO_2)_2C_2H_5$ (8)<br>$C_2H_5COCOC_2H_5$ (16)<br>$C_2H_5CO_2H$ (6) | 369 |
| $C_2H_5C(NO_2)=C(NO_2)C_2H_5$ | 85°/75 hr. | $C_2H_5C(NO_2)_2C(NO_2)_2C_2H_5$ (32) | 366 |
| $n\text{-}C_3H_7C\equiv CCH_3$ |  | Mixture of dinitroölefins (23) | 369 |
| (cyclohexene) | $N_2O_4$ to olefin in ether | (ring) NO₂, NO₂ (30)<br>(ring) OH*, NO₂ (54) | 352, 376 |
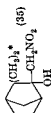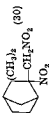
370

370, 363

627

| | |
|---|---|
| $N_2O_4/N_2$ | $(CH_3)_2$ / $CH_2NO_2$ (30) / $NO_2$ |
| | $(CH_3)_2$* / $CH_2NO_2$ (35) / $OH$ |
| | $(CH_3)_2$ / $CHNO_2$ (5) |
| $N_2O_4/O_2$ | $(CH_3)_2$ / $ONO_2$ (5) / $CH_2NO_2$ |
| | $COCH_2NO_2$ (22) / $C(CH_3)_2$ |
| | Nitro acids of unknown structure (39) |
| $n\text{-}C_4H_9CH=CH_2$ | $n\text{-}C_4H_9CHOHCH_2NO_2$* } mixture not separated<br>$n\text{-}C_4H_9CH(NO_2)CH_2NO_2$ ‡ |
| | $(CH_3)_2$ / $CH_3$ |

Note. References 385 to 631 are on pp. 371–376.
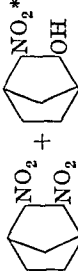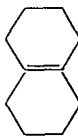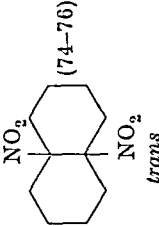
* The nitro alcohol is formed from the corresponding nitrite ester (CONO → COH) by hydrolysis, m working up the reaction mixture

‡ These products were not isolated. Their identity was inferred from hydrolysis and reduction products

## TABLE XIV—Continued

### A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes—Continued

| Olefin | Conditions | Product (%) | Refs. |
|---|---|---|---|
| (norbornene structure) | | (NO$_2$*/OH structure) + (NO$_2$/NO$_2$ structure) <br> exo-cis (16–22) trans (33–40) <br> trans (12–14) | 361 <br><br> 372 |
| CHCO$_2$C$_2$H$_5$ ‖ CHCO$_2$C$_2$H$_5$ | N$_2$O$_4$ to olefin in ether | ONOCHCO$_2$C$_2$H$_5$ ONOCHCO$_2$C$_2$H$_5$ + ONOCHCO$_2$C$_2$H$_5^+$ / ONOCHCO$_2$C$_2$H$_5$ / O$_2$NCHCO$_2$C$_2$H$_5$ | |
| (CH$_3$)$_3$CCH$_2$C(CH$_3$)=CH$_2$ | N$_2$O$_4$ to olefin in ether | (CH$_3$)$_3$CCH$_2$C(CH$_3$)(NO$_2$)CH$_2$NO$_2$ (30–44) <br> (CH$_3$)$_3$CCH$_2$C(CH$_3$)(OH)CH$_2$NO$_2$* (42–43) | 352, 376 |
| t-C$_4$H$_9$CH=C(CH$_3$)$_2$ | | t-C$_4$H$_9$CH(NO$_2$)C(CH$_3$)$_2$NO$_2$ (48) <br> t-C$_4$H$_9$CH(NO$_2$)C(CH$_3$)$_2$OH* (32) | 352, 376 |
| C$_6$H$_5$CH$_2$CH=CH$_2$ | N$_2$O$_4$/N$_2$ | C$_6$H$_5$CH$_2$CH(NO$_2$)CH$_2$NO$_2$ (34) <br> C$_6$H$_5$CH$_2$CHOHCH$_2$NO$_2$* (45) | 371 |
| C$_6$H$_5$CH$_2$CH=CH$_2$ | N$_2$O$_4$/O$_2$ | C$_6$H$_5$CH$_2$CH(ONO$_2$)CH$_2$NO$_2$ (13) <br> C$_6$H$_5$COCH$_2$NO$_2$ (20) <br> C$_6$H$_5$CH$_2$CHOHCH$_2$NO$_2$* (27) <br> C$_6$H$_5$CH$_2$CH(NO$_2$)CH$_2$NO$_2$ (4) | 371 |
| (decalin structure) | | (NO$_2$, NO$_2$ decalin structure) (74–76) trans | 361 |

370

370, 363

627

$c_6H_{11}$—$CH_3$

$N_2O_4/S_i$

$N_2O_4/O_2$



(CH₃)₃
CH₂NO₂
NO₂ (30)

(CH₃)₃
CH₂NO₃ (35)
OH

(CH₃)₃
CH=CHNO₂ (5)

ONO₂
CH₂NO₂ (5)

(COCH₃)NO₂ (22)

Nitro acids of unknown structure (30)

$n C_6H_5(CH(OH)CH_2NO_2^*)$  [mixture not separated]
$n C_6H_5(CH(NO_2)CH_2NO_2)$

(COCH₃)₂

(CH₃)₂

Note. References 315 to 631 are on pp. 351-356.
* The nitro alcohol is formed from the corresponding nitrite ester (CONO → COH) by hydrolysis, in working up the reaction mixture.
‡ These [yields] were not isolated   Their identity was inferred from hydrolysis and reduction products

TABLE XIV—*Continued*

*A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes—Continued*

| Olefin | Conditions | Product (%) | Refs. |
|---|---|---|---|
| $C_6H_5CH=CHCO_2C_2H_5$ | Ether/0° | $C_6H_5CH(ONO)CH(NO_2)CO_2C_2H_5$ or | 628 |
| $CH_2=CH(CH_2)_8CO_2H$ $C_6H_5C\equiv CC_6H_5$ | | $C_6H_5CH(NO_2)CH(NO_2)CO_2C_2H_5$ $C_6H_5CH(NO_2)CH(NO_2)CO_2C_2H_5$ $C_6H_5CH(NO_2)CH(ONO)CO_2C_2H_5$ $CH_2OHCH(NO_2)(CH_2)_8CO_2H*$ $C_6H_5(NO_2)C=C(NO_2)C_6H_5$ *trans* (19) *cis* (25) | 373 367 |
| | | $O_2N$ ... $C_6H_5$ ... $N \rightarrow O$ (6–7) + an intractable oil | |
| $C_6H_5CH=CHC_6H_5$ | $N_2O_4/N_2$ | $C_6H_5CH(NO_2)CH(NO_2)C_6H_5$ *meso* (21–25) ± (32–39) $C_6H_5CH(OH)CH(NO_2)C_6H_5$ *erythro* (9–10) *threo* (13–18) | 363, 362 |
| | $N_2O_4/O_2$ | $C_6H_5CH(ONO_2)CH(NO_2)C_6H_5$ (25) *erythro* (65) *threo* (35) $C_6H_5COCH(NO_2)C_6H_5$ (24) $C_6H_5CHOHCH(NO_2)C_6H_5$ (29) *erythro* and *threo* | 363 |
| $C_6H_5C\equiv CC\equiv CC_6H_5$ | $-25°$ | $C_6H_5(NO_2)C=C=C=C(NO_2)C_6H_5$ (34) | 368 |

n-C₇H₁₅CHOHCH₂NO₂ * (43)  
n-C₄H₉CH(NO₂)CH₂NO₂,NO₂ }(49)  624  
n-C₇H₁₅CH=CH·NO₂ }

B. Addition of Nitrosyl Chloride to Olefins and Acetylenes

| Olefin | Product (%) | Refs. |
|---|---|---|
| ClC≡CCl | Cl(NO₂)C=CCl₂ | 380 |
| CCl₂=CCl₂ | CCl₃CCl₂NO₂ | 379 |
| CF₂=CF₂ | CF₂CF₂NO₂ (57) | 365 |
| CCl₃—CHCl | CCl₃CHClNO₂ (79) | 383, 379 |
| CHCl₂—CHCl₂ | CHCl₂CHClNO₂ (67) | 379 |
| CHBr=CH₂ | CHClBrCH₂NO₂ (85) | 379 |
| CH₂=CH₂ | CH₂ClCH₂NO₂ (90) | 379 |
| CH₂=CHCN§ | O₂NCH₂CHClCN (76) | 377, 330 |
| | CH₄Cl₂CHClCN (14) | |
| CH₂=CHCN‖ | O₂NClCH₂CHClCN (25) | 377 |
| | CH₃CHClCHClCN (10) | |
| | O₂NCH—CHClN (48) | |
| CH₂—CHCH₂Cl | O₂NCH₂CHClCH₂Cl (61) | 629 |
| CH₂=CH—CH₂ | CH₂ClCHCl₂N₂O₂ (40–47) | 629, 630 |
| CH₃O₂CCH=CH₂ | CH₃O₂CCHClCH₂N₂O₂ (75) | 377, 369, 627 |
| | CH₃O₂CCHClCH₂Cl (7) | |
| CH₂=CHCH=CH₂—CH₂ | 1,2- and 1,4-Adducts and 1,2,3,4 bis adduct | |
| C₂H₅CH=CH₂ | CH₃CHClCH₂N₂O₂ (47) | 382 |
| CH₃CH=CHCH₃ | CH₂ClCHClCH₂N₂O₂, (25) | 629 |
| (CH₃)₂C=CH₂ | (CH₃)₂CClCH₂N₂O₂ (20–64) | 630 |
| n-C₅H₁₁CH=CH₂ | n-C₅H₁₁CHClCH₂N₂O₂ (46) | 629, 382, 630 |
| | n-C₅H₁₁CHClCH₂N₂O₂ (46) | 629 |

Note  References 385 to 631 are on pp. 371–376

* The nitro alcohol is formed from the corresponding nitrite ester (CONO → COH) by hydrolysis, in working up the reaction mixture.
§ No solvent was used.
‖ Either was used as solvent.
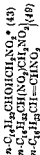
TABLE XIV—Continued

B. Addition of Nitryl Chloride to Olefins and Acetylenes—Continued

| Olefin | Product (%) | Refs. |
|---|---|---|
| (CH₃)₂CHCH=CH₂ | (CH₃)₂CHCHClCH₂NO₂ (47) | 629 |
| C₂H₅(CH₃)C=CH₂ | (CH₃)₂CHCHClCH₂Cl (26)<br>C₂H₅(CH₃)CClCH₂NO₂ (40) | 629 |
| cyclohexene | (structures) NO₂/Cl (42); Cl/Cl (27); Cl/ONO (13)¶; NO₂/ONO (5)** | 358, 630, 379 |
| n-C₄H₉CH=CH₂ | n-C₄H₉CHClCH₂NO₂ (42) | 629 |
| n-C₃H₇(CH₃)C=CH₂ | n-C₃H₇(CH₃)CClCH₂NO₂ (35) | 629 |
| (CH₃)₂CHCH₂CH=CH₂ | (CH₃)₂CHCH₂CHClCH₂NO₂ (41) | 629 |
| (CH₃)₂C=CHOCOCH₃ | (CH₃)₂CClCHO (21) ††<br>(CH₃)₂C(NO₂)CHO (12) | 631 |
| n-C₅H₁₁CH=CH₂ | n-C₅H₁₁CHClCH₂NO₂ (39) | 629 |
| C₆H₅C≡CH | C₆H₅CCl=CHNO₂ (34)<br>C₆H₅COCHCl₂ (9)<br>C₆H₅C(NO₂)=CHCl (—)<br>C₆H₅C(NO₂)₂CHCl₂ (—) | 369<br>383, 379 |
| C₆H₅CH=CH₂ | C₆H₅CH(NO₂)CH₂Cl (—) | 379 |
| C₆H₅CH=CHCO₂H | C₆H₅CH(NO₂)CHClCO₂H (43) | 383, 379 |
| C₆H₅C(OCOCH₃)=CH₂ | C₆H₅COCH₂NO₂ (36)††<br>C₆H₅COCH₂Cl (14) | 631 |
| C₆H₅C(OCOCH₃)=CHCH₃ | C₆H₅COCH(NO₂)CH₃ (28) | 631 |
| C₆H₅CH=CHC₆H₅ | C₆H₅CHClCH(NO₂)C₆H₅ (27) | 379 |

## C. Addition of $N_2O_4/X_2$ to Olefins and Acetylenes

| Olefin | Addendum | Product (%) | Refs |
|---|---|---|---|
| $CHCl=CCl_2$ | $Cl_2N_2O_4$ | $CCl_2ClCHClNO_3$ (5) | 375 |
| | | $CCl_3CHCl_2$ (8) | 375 |
| $CH_2=CCl_2$ | $Cl_2N_2O_4$ | $CCl_2=CClNO_2$ (4) | 375 |
| | | $CCl_3CH_2NO_2$ (40) | 375 |
| | | $CCl_3CH_2Cl$ (2) | 375 |
| | $Br_2N_2O_4$ | $CCl_3BrCH_2NO_2$ (25) | 375 |
| | | $CCl_3BrCH_2Br$ (9) | 375 |
| $CHCl=CHCl$ | $Cl_2N_2O_4$ | $CHCl_2CHClNO_3$ (7) | 375 |
| | | $CHCl_2CHCl_2$ (3) | 375 |
| $CH_2=CHBr$ | $Cl_2N_2O_4$ | $CHClBrCH_2NO_3$ (41) | 375 |
| | | $CH_3CHClBr$ (32) | 375 |
| | $Br_2N_2O_4$ | $CHBr_2CH_2NO_3$ (35) | 375 |
| | | $CH_2BrCHBr_2$ (58) | 375 |
| $CH_2=CHCl$ | $Cl_2N_2O_4$ | $CHCl_2CH_2NO_3$ (36) | 375 |
| | $Br_2N_2O_4$ | $CHClBrCH_2NO_3$ (28) | 375 |
| | | $CHClBrCH_2Br$ (24) | 375 |
| | $Cl_2N_2O_4$ | $CHClCH_2NO_3$ (69) | 381 |
| $CH_2=CHCN$ | $Cl_2N_2O_4$ | $CH_2(NO_3)CH_2Cl$ (24) | 375 |
| $CH_3CH=CHCl$ | $Cl_2N_2O_4$ | $CH_3CH(NO_3)CH_2Cl$ (14) | 375 |
| $CH_3CH=CH_2$ | $I_2N_2O_4$ | $CH_3CHClCH_2Cl$ (45) | 360 |
| | $I_2N_2O_4$ | $CH_2ClCHClCH_2Cl$ (70) | 360 |
| $CH_2=CHCOCH_3$ | | $O_2NCH_2CHClCOCH_3$ (75) | |

Note. References 365 to 631 are on pp. 371-376.
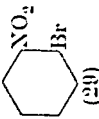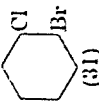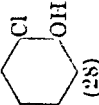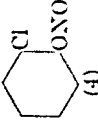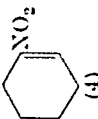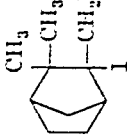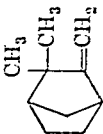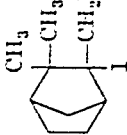
¶ The product was not isolated. After hydrolysis a mixture of about equal parts 1-chloro-2-cyclohexanol and 1-chloro-2-cyclohexanol nitrate was obtained

** 1-Nitro-2-cyclohexanol was isolated

†† These products were obtained after hydrolysis.

TABLE XIV—*Continued*

C. *Addition of N₂O₄/X₂ to Olefins and Acetylenes—Continued*

| Olefin | Addendum | Product (%) | Refs. |
|---|---|---|---|
| $C_2H_5CH=CH_2$ | $Cl_2/N_2O_4$ | $C_2H_5CH(NO_2)CH_2Cl$ (9) | 381 |
|  | $I_2/N_2O_4$ | $C_2H_5CHClCH_2NO_2$ (62) | 360 |
| (cyclohexene) | $N_2O_4/BrCCl_3$ | (Br, NO₂) (29); (Br, Cl) (31); (Cl, OH) (28); (Br, ONO₂) (4); (NO₂) (4) | 358, 357 |
| $CH_3C(OCOCH_3)=CHCH_3$ | $Cl_2/N_2O_4$ | $CH_3COCHClCHCH_3$ (58) | 375 |
|  | $Br_2/N_2O_4$ | $CH_3COCHBrCHCl_3$ (50) | 375 |
|  | $I_2/N_2O_4$ | $CH_3COCHI_2CH_3$ (34); $CH_3COCOCH_3$ (23) | 375 |
| $C_6H_5C{\equiv}CH$ | $I_2/N_2O_4$ | $C_6H_5CI=CHNO_2$ (86) (single isomer) | 360 |
| (bicyclic CH₃, CH₃, =CH₂) | $I_2/N_2O_4$ | (bicyclic CH₃, CH₃, CH₂NO₂, I) (50) | 360 |
| $C_6H_5C{\equiv}CC_6H_5$ | $I_2/N_2O_4$ | $C_6H_5CI=C(NO_2)C_6H_5$ *trans* (66); *cis* (15) | 360 |
| *trans*-$C_6H_5CH=CHC_6H_5$ | $I_2/N_2O_4$ | $C_6H_5CH(NO_2)CHIC_6H_5$ (96)‡‡ | 360 |
| *cis*-$C_6H_5CH=CHC_6H_5$ | $I_2/N_2O_4$ | $C_6H_5CH(NO_2)CHIC_6H_5$ (63)‡‡ | 360 |

*Note:* References 385 to 631 are on pp. 371–376.

‡‡ The same adduct (a single isomer) was obtained from both *cis*- and *trans* stilbene. It is stated that it is probably the *erythro* isomer.

# REFERENCES FOR TABLES IX-XIV

[385] Haszeldine and Steele, *J. Chem. Soc.*, **1954**, 3747

[386] Leitch and Morse, *Can. J. Chem.*, **29**, 1034 (1951)

[387] Haszeldine and Osborne, *J. Chem. Soc.*, **1958**, 61.

[388] Kharasch, McNab, and Mayo, *J. Am. Chem. Soc.*, **55**, 2521 (1933).

[389] Verhulst and Jungers, *Bull. Soc. Chim. Belges*, **58**, 73 (1949).

[390] Kharasch and Hannum, *J. Am. Chem. Soc.*, **56**, 712 (1934).

[391] Vaughan and Rust, *Brit. pat.* 554,499, *U.S. pat.* 2,307,552 [*C. A.*, **37**, 3452 (1943)]

[392] Haszeldine, *J. Chem. Soc.*, **1953**, 3559

[393] Haszeldine and Steele, *J. Chem. Soc.*, **1955**, 3005.

[394] Henne and Nager, *J. Am. Chem. Soc.*, **73**, 5527 (1951).

[395] Haszeldine, *J. Chem. Soc.*, **1952**, 2504

[396] Kharasch, McNab, and Mayo, *J. Am. Chem. Soc.*, **55**, 2531 (1933).

[397] Kharasch and McNab, *J. Am. Chem. Soc.*, **56**, 1425 (1934)

[398] Rust and Vaughan, *J. Org. Chem.*, **7**, 491 (1942).

[399] den Hertog and Brain, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **54B**, 379 (1951) [*C. A.*, **47**, 2121 (1953)]

[400] Kharasch, Margolis, and Mayo, *J. Org. Chem.*, **1**, 393 (1936)

[401] Walling, Kharasch, and Mayo, *J. Am. Chem. Soc.*, **61**, 2693 (1939)

[402] Grimshaw, Guy, and Smith, *J. Chem. Soc.*, **1940**, 68

[403] Goering and Larsen, *J. Am. Chem. Soc.*, **79**, 2653 (1957)

[404] Kharasch and Hinckley, *J. Am. Chem. Soc.*, **56**, 1212 (1934)

[405] Kharasch and Hinckley, *J. Am. Chem. Soc.*, **56**, 1243 (1934)

[406] Kharasch and Potts, *J. Am. Chem. Soc.*, **59**, 57 (1932)

[407] Khrunyants and Cheburkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci (Engl. Transl)*, **1960**, 2007.

[408] Kharasch and McNab, *Chem. & Ind. (London)*, **54**, 989 (1935).

[409] Price and Coyner, *J. Am. Chem. Soc.*, **62**, 1306 (1940).

[410] Kharasch, Hinckley, and Gladstone, *J. Am. Chem. Soc.*, **56**, 1642 (1934).

[411] Kharasch, Walling, and Mayo, *J. Am. Chem. Soc.*, **61**, 1559 (1939).

[412] Michael and Weiner, *J. Org. Chem.*, **5**, 389 (1940).

[413] Sommer, Bailey, Goldberg, Buck, Bye, Evans, and Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

[414] Walborsky and Schwarz, *J. Am. Chem. Soc.*, **75**, 3241 (1953)

[415] Golmov, *J. Gen. Chem. USSR (Engl. Transl)*, **22**, 2187 (1952).

[416] Kharasch, Hannum, and Gladstone, *J. Am. Chem. Soc.*, **56**, 244 (1934)

[417] Kharasch and Fuchs, *J. Org. Chem.*, **10**, 159 (1945).

[418] Quelet, Durand Dran, and Fuseau, *Compt. Rend.*, **244**, 1218 (1957).

[419] Dadießle, Fritach, Baranger, and Schalbar, *Compt. Rend.*, **244**, 2402 (1957).

[420] Ashton and Smith, *J. Chem. Soc.*, **1934**, 435.

[421] Abraham, Mowat, and Smith, *J. Chem. Soc.*, **1937**, 948.

[422] Jungermann and Spoerri, *J. Am. Oil Chemists' Soc.*, **35**, 293 (1958).

[423] Leitch and Morse, *Can. J. Chem.*, **30**, 924 (1952).

[424] Hanford and Harmon, *U.S. pat.* 2,418,832 [*C. A.*, **42**, 581 (1948)]

[425] Hoshino, Yamaguhil, and Ichikawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 510 (1953) [*C. A.*, **48**, 5789 (1954)].

[426] Brubaker, *U.S. pat.* 2,680,763 [*C. A.*, **49**, 9991 (1955)]

[427] Vander Weele, *U.S. pat.* 2,521,617 [*C. A.*, **45**, 1161 (1951)]

[428] Passon and Tahler, *U.S. pat.* 2,626,933 [*C. A.*, **45**, 7358 (1951)]

[429] Cunningham and Beach, *U.S. pat.* 2,626,282 [*C. A.*, **48**, 709 (1954)].

[430] Litvak and Britton, *U.S. pat.* 2,557,913 [*C. A.*, **46**, 1593 (1952)].

[431] Dow Chemical Co., *Brit. pat.* 587,484 [*C. A.*, **47**, 9998 (1953)].

478 Burkhard, J Am Chem Soc, 72, 1078 (1950).

489 British Thomson Houston Co, Brit pat 638,408 [C A, 48, 10035 (1954)].

480 Henkel and Cie, G m b H, pat 470,717 [C A, 32, 593 (1938)].

481 Bluestone, Soloway, Hyman, and Lalov, U S pat 2,782,238 [C A, 51, 8132 (1957)].

482 Smith and Hartmann, Acta Chem Scand, 3, 1111 (1954).

483 Cadogan and Hey, Quart Rev (London), 5, 308 (1951).

484 Koenig and Swern, J Am Chem Soc, 79, 362 (1957).

485 Fote, O Connor, and Goldblatt, J Am Oil Chemists' Soc, 35, 225 (1958).

486 Burkhard, U S pat 2,663,516 [C A, 48, 1580 (1951)].

487 British Thomson Houston Co, Brit pat 684,993 [C A, 47, 4358 (1953)].

488 Burke and Huffman, U S pat 2,515,835 [C A, 44, 8943 (1950)].

489 Holmberg, Arkiv Kemi Mineral Geol, 15A, No 21 (1942).

490 Hanna, J Am Chem Soc, 74, 2120 (1952).

491 Hendrickson and Hatch, J Org Chem, 25, 1747 (1960).

492 Schwab, J Am Chem Soc, 78, 623 (1954).

493 Jacobson, U S pat 2,439,212 [C A, 42, 5041 (1948)].

494 Coffman, U S pat 2,347,182 [C A, 39, 226 (1945)].

495 Reppe and Nicolai, U S pat 2,073,589 [C A, 31, 3065 (1937)].

496 I G Farbenind, Brit pat 442,607 [C A, 30, 4694 (1936)].

497 Saam, Longe, Birger, DeSantis, and Saam, J Org. Chem, 26, 3538 (1961).

498 Cupmoon, Rubber Chem Technol, 28, 370 (1955).

499 Marvel and Nowlin, J Am Chem Soc, 72, 5028 (1950).

500 Marvel and Baumgarten, J Polymer Sci, 6, 127 (1951).

501 Marvel and Cripps, J Polymer Sci, 9, 53 (1952).

502 Posner, Ber, 40, 4788 (1907).

503 Alexander and McCombie, J Chem Soc, 1931, 1913.

504 Goering, Relyea, and Howe, J Am. Chem Soc, 79, 2507 (1957).

505 Reppe and Ufer, Ger, pat 636,077 [C A, 31, 704 (1937)].

506 I G Farbenind, Fr pat 783,884 [C A, 29, 8355 (1935)].

507 Carothers, J Am Chem Soc, 55, 2008 (1933).

508a Lester, Rodgers, and Reid, J Am. Chem Soc, 66, 1674 (1944).

509 N. V. Bataaf Pet. Maats, Brit. pat 680,637 [C A, 48, 4581 (1954)].

510 Peppel, U S pat 2,408,095 [C.A , 41, 778 (1947)].

511 Sjoberg, Ber, 74, 64 (1941).

512 Bordwell and Hewett, J. Org Chem, 23, 636 (1958).

513 Lazier, Pavlic, and Peppel, U S pat 2,422,246 [C A, 41, 6277 (1947)].

514 Fredga and Martensson, Arkiv Kemi Mineral Geol, 16B, No. 8 (1943).

515 Farlow, U S pat 2,406,362 [C A, 42, 7233 (1946)].

516 Farlow, Brit pat 592,631 [C A, 42, 2277 (1948)].

517 Schubert and Wagner, Naturwiss, 34, 189 (1947).

518 Schönberg, Gerell Kem Tidskr, 53, 282 (1941) [C A, 36, 1902 (1942)].

519 N P Neureiter, Doctoral Dissertation, Northwestern University, 1957, Dissertation Abstr, 18, 401 (1958).

520 Behringer, Ann, 564, 219 (1949).

521 Statesmen and Glazebrook, J Chem Soc, 1958, 2834.

522 Vinton, U S pat 2,427,582 [C A, 42, 212 (1948)].

523 Morago, McPherson, and Folkers, Brit pat 638,513 [C A, 44, 8306 (1950)].

524 Vinton, U S pat 2,607,776 [C A, 47, 6993 (1953)].

525 Holmberg, Arkiv Kemi Mineral Geol, 12B, No 17 (1938) [C A, 32, 4131 (1938)].

526 Bateman and Glazebrook, Chem et Ind (London), 1951, 1093.

527 Bateman, Glazebrook, Moore, Porter, Ross, and Saville, J Chem Soc, 1958, 2838

528 Langhammer, U S pat 2,402,690 [C A, 40, 5850 (1946)].

529 Knuth, Bavley, and Lazier, J Org Chem, 19, 845 (1954)

530 Bateman, Glazebrook, and Moore, J Chem Soc, 1958, 2848

531 Glazebrook and Saville, J Chem Soc, 1954, 2094.

[531] Schlack, Ger. pat. 896,802 [C.A., 49, 3242 (1955)].

[532] Koenig, Sasin, and Swern, J. Org. Chem., 23, 1525 (1958).

[533] C. M. Barringer, Doctoral Dissertation, Princeton University, 1950; Dissertation Abstr., 15, 341 (1955).

[534] Mel'nikov and Shvetsova-Shilovskaya, Doklady Akad. Nauk SSSR, 86, 543 (1952) [C.A., 48, 556 (1954)].

[535] Vladimirova and Mel'nikov, J. Gen. Chem. USSR (Engl. Transl.), 26, 2861 (1956).

[536] Bacon and LeSuer, J. Am. Chem. Soc., 76, 670 (1954).

[537] Bacon, Meinhardt, and LeSuer, J. Org. Chem., 25, 1993 (1960).

[538] Fields, J. Org. Chem., 21, 497 (1956).

[539] Brooks, Howard, and Wehrle, J. Am. Chem. Soc., 72, 1289 (1950).

[540] Cairns and Sauer, U.S. pat. 2,776,995 [C.A., 51, 9679 (1957)].

[541] Liu and Wang, K'o Hsüeh T'ung Pao, 1957, 206 [C.A., 53, 9115 (1959)].

[542] Holmberg, Arkiv Kemi, 2, 567 (1950) [C.A., 46, 100 (1952)].

[543] Arens, Hermans, and Weiland, Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B, 58, 78 (1955) [C.A., 50, 1582 (1956)].

[544] Arens, Volger, Doornbos, Bonnema, Greidanus, and van den Hende, Rec. Trav. Chim., 75, 1459 (1956).

[545] Volger and Arens, Rec. Trav. Chim., 77, 1170 (1958).

[546] Boonstra, Brandsma, Wiegman, and Arens, Rec. Trav. Chim., 78, 252 (1959).

[547] Bogdanova, Shostakovskiĭ, and Plotnikova, Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.), 120, 337 (1958).

[548] Bonnema and Arens, Rec. Trav. Chim., 79, 1137 (1960).

[549] Shostakovskiĭ, Bogdanova, Plotnikova, and Andreer, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1960, 1185.

[550] Shostakovskiĭ, Bogdanova, and Plotnikova, Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.), 124, 21 (1959).

[551] Prilezhaeva, Guseinov, Lopatin, and Shostakovskiĭ, J. Gen. Chem. USSR (Engl. Transl.), 29, 3190 (1959).

[552] Miles and Owen, J. Chem. Soc., 1952, 817.

[553] Walborsky, Davis, and Howton, J. Am. Chem. Soc., 73, 2590 (1951).

[554] Kohler and Potter, J. Am. Chem. Soc., 57, 1316 (1935).

[555] Baker and Querry, J. Org. Chem., 15, 417 (1950).

[556] Vaughan and Rust, U.S. pat. 2,398,480 [C.A., 40, 3766 (1946)].

[557] Gabriel and Eschenbach, Ber., 30, 2497 (1897).

[558] Vaughan and Rust, U.S. pat. 2,398,479 [C.A., 40, 3765 (1946)].

[559] Vaughan and Rust, Brit. pat. 581,775 [C.A., 41, 2999 (1947)].

[560] Evans, Vaughan, and Rust, U.S. pat. 2,376,675 [C.A., 39, 3533 (1945)].

[561] K. L. Howe, Doctoral Dissertation, University of Wisconsin, 1957; Dissertation Abstr., 17, 1215 (1957).

[562] Shostakovskiĭ, Shapiro, and Sidel'korvkaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1958, 60.

[563] N. V. Bataaf. Pet. Maats., Fr. pat. 955,001 [C.A., 45, 6834 (1951)].

[564] Vaughan and Rust, U.S. pat. 2,411,983 (1946).

[565] Akashi, Hanabusa, and Oda, J. Chem. Soc. Japan, 57, 447 (1954) [C.A., 49, 15724 (1955)].

[566] Barrick, U.S. pat. 2,403,207 [C.A., 40, 6497 (1946)].

[567] Wicklatz, U.S. pat. 2,600,287 [C.A., 47, 1726 (1953)].

[568] Rosenthal, Ann., 233, 15 (1886).

[569] Müller, Ber, 6, 1441 (1873).

[570] Marckwald and Frahne, Ber., 31, 1854 (1898).

[571] Miller, Ann., 189, 338 (1877).

[572] N. V. Bataaf. Pet. Maats., Brit. pat. 661,771 [C.A., 46, 9120 (1952)].

[573] Labbé, Bull. Soc. Chim. France, (3) 21, 1077 (1899).

[574] Ufer and Hecht, Ger. pat. 698,272 [C.A., 35, 6600 (1941)].

[575] I. G. Farbenind, Fr. pat. 858,185.

578 Gilman and Hewlett, *Iowa State Coll J Sci*, 5, 19 (1930) [*C A*, 25, 4263 (1931)].

577 Akashi, Hanabusa, and Oda, *J Chem. Soc. Japan, Ind Chem Sect*, 56, 718 (1953) [*C.A.*

49, 7545 (1955)].

578 Luttringhaus, Schmidt, and Alpes, *Angew. Chem*, 69, 138 (1957)

579 British Thomson-Houston Co, Brit pat 661,094 [*C A*, 46, 6365 (1951)].

580 Midland Silicones, Ltd, Brit pat 771,587 [*C A*, 51, 13904 (1957)].

581 Kruble, U S pat 2,524,529 [*C A*, 45, 2018 (1951)].

582 MacKenzie, Spalter, and Schoffman, U S pat 2,721,873 [*C.A.*, 45, 7844 (1956)].

583 Barry, DePree, and Hook, Brit. pat 633,732 [*C A*, 45, 3409 (1951)].

584 Shostakovskii and Shmonina, *Bull Acad Sci. USSR, Div. Chem Sci (Engl Transl.)*,

1958, 56.

585 Calas, Duffaut, and Valade, *Bull Soc Chim France*, 1955, 790

586 Voronkov and Romanova, *J. Gen Chem USSR (Engl. Transl.)*, 28, 2161 (1958).

587 Topchiev, Nametkin, and Chernysheva, *Proc. Acad. Sci. USSR, Chem. Sect (Engl.

Transl.)*, 115, 741 (1957)

588 Kanarzala, *Bull. Chem Soc. Japan*, 26, 493 (1953).

589 Kanazawa and Ino, *Jap pat* 5645 [*C A*, 49, 14377 (1955)].

590 Hatcher and Bunnell, U S pat 2,545,780 [*C.A.*, 45, 7500 (1951)].

591 Speier, U S pat 2,723,987 [*C A*, 50, 10123 (1956)]

592 Calas, Frannet, and Valade, *Bull. Soc. Chim. France*, 1952, 241.

593 Calas and Frannet, *Bull Soc Chim. France*, 5, 6 (1956) [*C A*, 50, 12990 (1956)].

594 Calas and Duffaut, *Bull Soc Chim. France*, 1952, 792.

595 Calas and Duffaut, *Oléagineux*, 8, 21 (1953) [*C A*, 47, 12223 (1953)].

596 Calas and Duffaut, *Bull Soc Chim. France*, 1953, 792.

597 Mironov and Petrov, *Bull Acad. Sci. USSR, Div. Chem Sci (Engl Transl)*, 1958, 767.

598 Barry, DePree, and Hook, U S pat 632,324 [*C A*, 44, 5373 (1950)].

599 Hurd, U S pat 2,527,703 [*C A*, 45, 3409 (1951)]

600 Midland Silicones, Ltd , Brit. pat 769,497 [*C.A.*, 52, 430 (1958)].

601 Speier, U S pat 2,762,823 [*C A*, 51, 7419 (1957)].

602 Topchiev, Nametkin, and Chernyshova, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl.

Transl.)*, 118, 97 (1958).

603 Gilman, Miles, Moore, and Gerow, *J. Org Chem*, 24, 219 (1959)

604 Calas and Duffaut, *Bull. Chem. Assoc. Inform. ITERG*, 7, 438 (1953) [*C.A.*, 48, 11303 (1954)].

605 Nesmeyanov, Freidlina, and Chukovskaya, *Proc. Acad. Sci USSR, Chem. Sect. (Engl.

Transl.)*, 115, 785 (1957).

606 Gabsby, *Research (London)*, 3, 338 (1950)

607 Kruble, U S pat 2,510,842 [*C.A.*, 45, 1473 (1950)]

608 Kruble, U S pat 2,510,853 and pat 684,507 [*C.A.*, 48, 2761 (1954)]

609 MacKenzie, Spalter, and Schoffman, Brit. pat 684,507 [*C.A.*, 48, 2761 (1954)]

609 Kruble, U S pat 2,582,568 [*C.A.*, 52 Naturforsch, 11b, 115 (1956)]

610 Sternschneider, Menge, and Klang, *Z Naturforsch*, 11b, 115 (1956)

611 Fisher, West, and Rochow, *J. Am Chem Soc*, 76, 5878 (1954)

612 Ladd and Harvey, U S pat 2,510,699 [*C.A.*, 44, 7348 (1950)].

613 Kharasch, U S pat 2,489,091 [*C A*, 44, 6046 [*C.A.*, 51, 4416 (1957)].

614 Kharasch, U S pat 2,842,560 [*C A*, 53, 19838 (1959)]

615 Ziegler, Deparade, and Meyer, U S pat 2,842,566 [*C A*, 53, 19838 (1959)]

616 Nozaki, U S. pat 2,863,885 [*C.A.*, 52, 2049 (1958)]

617 Stiles, Rust, and Vaughan, U S pat 2,803,597 [*C.A.*, 48, 9590 (1952)]

618 Brown, U S pat 2,684,112 [*C A*, 48, 8590 (1954)]

619 Pudovik, Moshkina, and Konovalova, *J. Gen. Chem. USSR (Engl. Transl.)*, 29, 3301

(1959).

619α V. Estzaf Pat. Maats, Dutch pat. 69,357 [*C.A.*, 47, 143 (1953)]

619b Linville, U S pat. 2,843,615 [*C.A.*, 53, 1147 (1959)]

620 Lanvile, Ger pat. 1,000,210

621 Lanvile, Ger pat. Brit pat 694,772 [*C A*, 49, 4705 (1955)]

622 United States Rubber Co , U S pat 2,664,438 [*C A*, 48, 13711 (1954)]

623 Ladd and Harvey, U S pat 2,664,495 [*C A*, 48, 13711 (1954)]

624 E. I du Pont de Nemours and Co , Brit pat. 603,344 [*C A*, 42, 665 (1948)].

[624] Porter and Wood, *J. Inst. Petrol.*, **38**, 877 (1952).

[625] Vasil'ev, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 3380 (1960).

[626] Weghofer, *Rev. Quim. Ind. (Rio de Janeiro)*, **22**, 114 (1953) [*C.A.*, **48**, 11295 (1954)].

[627] Porter and Wood, *J. Inst. Petrol.*, **37**, 388 (1951).

[628] Vasil'ev and Vouchenko, *J. Gen. Chem. USSR (Engl. Transl.)*, **20**, 1283 (1950).

[629] Villo and duPont, *Bull. Soc. Chim. France*, **1956**, 804.

[630] Price and Sears, *J. Am. Chem. Soc.*, **75**, 3275 (1953).

[631] Bachman and Hokama, *J. Org. Chem.*, **25**, 178 (1960).

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